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TEXTILE RESEARCH JOURNAL

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IN THIS ISSUE

SECOND-ORDER TRANSITION TEMPERATURE AND FIBER PROPERTIES. Alexander Brown 891

A STUDY OF BLENDED WOOLEN STRUCTURES. *PART II:* BLEND DISTRIBUTION IN SOME WOOL–NYLON AND WOOL–VISCOSE YARNS. Myron J. Coplan and Manfred G. Bloch 902

PENETRATION OF ALKALINE SOLUTIONS INTO WOOL FIBERS DETERMINED BY CHANGES IN THE RIGIDITY MODULUS. Märianne Kärrholm, Gösta Nordhammer, and Ove Friberg 922

A STUDY OF THE ALCOHOLYSIS OF CELLULOSE. Richard B. Valley . 930

THE RELATION OF SINGLE-FIBER TO FLAT-BUNDLE STRENGTH AND ELONGATION OF COTTON. Rollin S. Orr, Louis C. Weiss, and James N. Grant 939

STRESS RELAXATION OF FIBERS AS A MEANS OF INTERPRETING PHYSICAL AND CHEMICAL STRUCTURE. *PART I:* DETERMINATION OF THE RELATIVE ACCESSIBILITY OF FIBERS. T. Lemiszka and J. C. Whitwell 947

THE SORPTION OF HCl BY TEXTILE FIBERS. *PART II:* SORPTION OF MODIFIED WOOL FIBERS AND OTHER FIBERS. P. Larose . . . 956

THE BREAKING OF SINGLE COTTON FIBERS UNDER VARIOUS CONDITIONS. Ray L. Pearson, Albert G. Funk, and Henry Eyring 961

THE OXIDATION OF WOOL BY INORGANIC PERACIDS. Christopher Earland, Thomas P. MacRae, Gordon J. Weston, and Kenneth Statham . . 963

Letters to the Editor

BEHAVIOR OF YARNS SUBJECT TO IMPACT LOADING. I. J. Gruntfest 966

CORRELATION OF THE PHYSICAL PROPERTIES OF JUTE YARN WITH THE CHEMICAL CHARACTERISTICS OF THE FIBER. S. B. Bandyopadhyay and S. K. Mukhopadhyay 967

Correction 968

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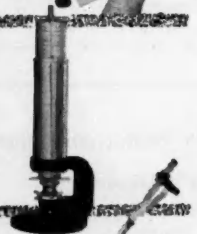

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TEXTILE RESEARCH JOURNAL

VOL. XXV, NO. 11 NOVEMBER 1955

Second-Order Transition Temperature and Fiber Properties[1]

Alexander Brown[2]

Carbide & Carbon Chemicals Company, South Charleston, W. Va.

Introduction

While the second-order transition temperature and its associated effects are of extreme importance in the field of the mechanical behavior of high polymers, little of the considerable literature on the subject has appeared in journals primarily concerned with textiles. This presentation, therefore, will be primarily a discussion of the nature of the second-order transition temperature and its associated effects on fiber properties, with some new experimental results included for illustration.

Experimental

The effect of second-order transition temperature on the two fiber properties of stiffness and resiliency was measured in this study. Most of the fibers were in the form of low-twist continuous-filament yarns, although some were staple yarns or single fibers. An Instron Tensile Tester was used throughout, with the fiber sample suitably enclosed by a heating oven. Generally 2-in. gauge length samples were used, and these were mounted in specially made jaws equipped with adaptors for attachment to the load cell and movable crosshead of the instrument. Figures 1, 2, and 3 show the method of sample mounting, the oven, and the testing assembly.

In operation the fiber sample is stretched at an extension rate of 0.2 in./min until an extension of 1.2 to 1.3% is attained. The crosshead travel is immediately reversed and returned to the starting point at the same 0.2 in./min rate. The sample is allowed to rest untensioned for 1 min; then the process is repeated for a check. The temperature is recorded by a thermocouple and then is raised to a higher value by adjustment of a Variac connected to the heater coils of the oven. Once temperature equili-

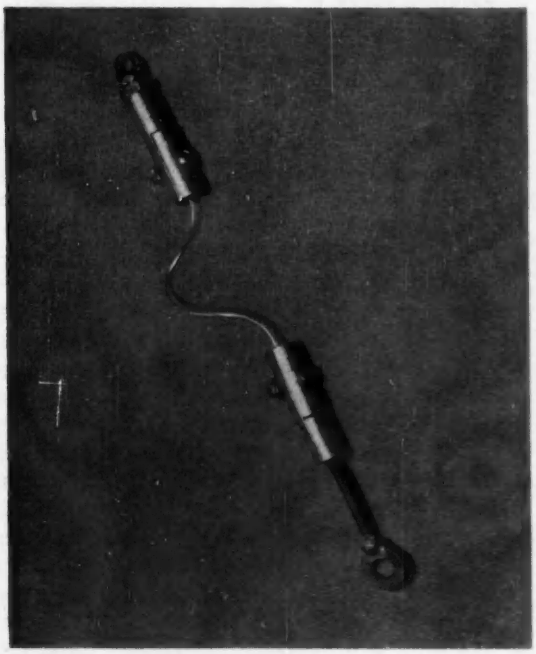

Fig. 1. Yarn sample in jaws.

[1] Presented at the Gordon Conference on Textiles, July 10, 1954.

[2] Present address, Research Department, Bakelite Company, Bloomfield, New Jersey.

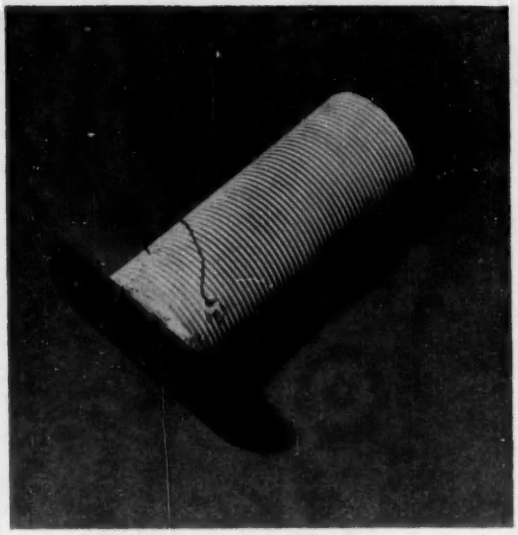

Fig. 2. Heating oven.

brium is attained at this higher temperature, a period of about 3 min being usual, the stretching and recovery process is repeated at this higher temperature. This procedure is followed until the desired temperature range has been covered. The whole range can be covered using the same sample. Apparently no objectionable mechanical history is impressed on the sample by the small stretches; the progressive heating to higher temperatures effectively wipes it out. Spot checks with new samples at a single temperature reveal essentially the same mechanical behavior as that of the single sample carried throughout the temperature range.

The record obtained consists of a series of load-elongation cycles, to about 1.3% extension, at progressively higher temperatures. One such cycle is reproduced in Figure 4. From the measured gauge length of the sample the elongation corresponding to a 1.00% stretch is calculated. The load at this elongation on the diagram, *O*, is multiplied by 100 and divided by the denier of the sample to yield the stiffness. The ratio *CD/AD* multiplied by 100 is arbitrarily defined as the resiliency of the sample.

The sample length is chosen to conform with the dimensions of the oven. The denier of the sample is chosen such that most, or all, of the wide range of stiffness expected over the temperature range can be measured with suitable sensitivity by the load-selector switch and one load cell.

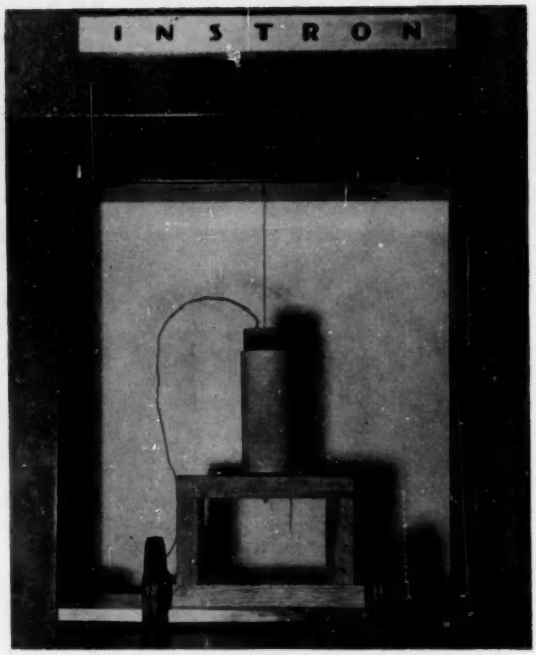

Fig. 3. Testing assembly.

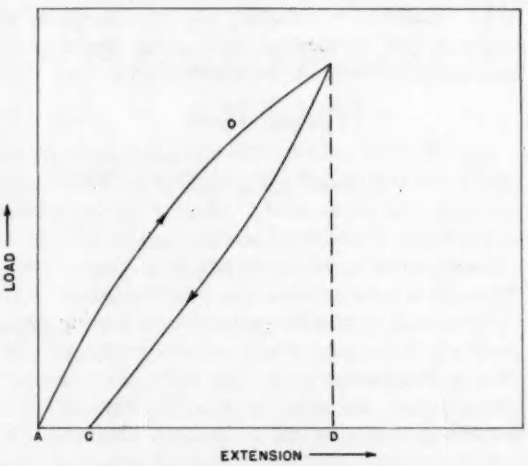

Fig. 4. Typical load-elongation cycle.

Stiffness-Temperature Behavior

There are a number of effects that occur in high polymers at the second-order transition temperature, and each of them offers a specific definition of second-order transition temperature. It is convenient to

begin with one such effect and definition and then develop by stages until a basic general definition is reached.

One of the effects noted in plastics at the second-order transition temperature is that the system changes from brittle to flexible. Using plastics nomenclature, then, the second-order transition temperature of a polymer could be defined as the brittle-point temperature of the polymer. Above the second-order transition temperature the system is soft and extensible; below the second-order transition temperature the system is brittle, hard, and stiff. In fibers we are not normally concerned with brittleness; however, we are concerned with stiffness. Figure 5 shows the change in stiffness that occurs in acetate rayon as it is heated through its second-order transition temperature. This temperature is about 180°C.

The first thing to note here is the range of stiffnesses measured on this system. The measured values ranged from about 35 g/den at room temperature down to 0.1 g/den at 200°C, which necessitates the use of logarithmic stiffness as the ordinate. Second, the form of the stiffness temperature curve should be noted. Over a considerable temperature range, from about room temperature to about 160°C, there is little drop in stiffness. Then the stiffness starts to drop more and more rapidly with increasing temperature, and, over the last few degrees covered, the stiffness is dropping almost perpendicularly. Also, while this drop in stiffness is very rapid, one cannot unequivocally describe a particular temperature at which it occurs. There are no discontinuities in the curve. The big effect, in stiffness, is noted as occurring on either side of a temperature range. This fiber at 200°C, where it exihibts the stiffness of 0.1 g/den, is, for textile consideration, melted. (The fiber still looks like a fiber but it is sticky.) The above offers the first modification of the simple definition of second-order transition temperature. It was first stated that it was the temperature at which the system changed from a brittle material to a soft one. Now, with the results on this polymer system, second-order transition temperature might be defined as the melting point of the system, bearing in mind the general broadness of high-polymer melting points.

Figure 6 shows the stiffness-temperature behavior of Dacron (polyethylene terephthalate).[3] Instead

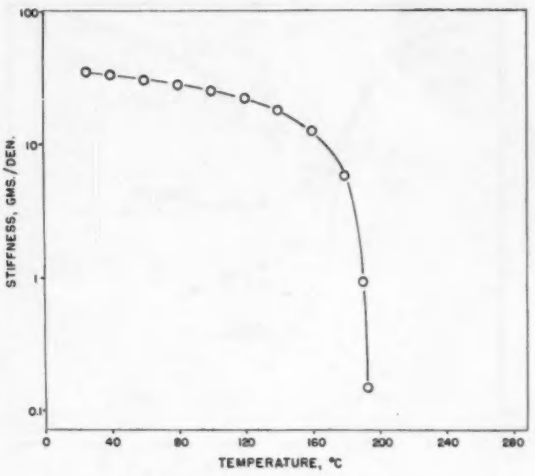

Fig. 5. Stiffness-temperature behavior of acetate rayon.

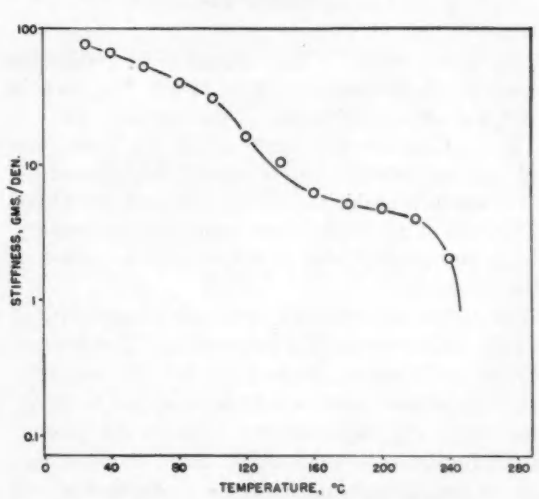

Fig. 6. Stiffness-temperature behavior of Dacron.

of a single drop-off in stiffness, as is shown by acetate rayon, the Dacron behavior exhibits two, one a gradual drop in the region of 60 to 100°C, followed by a more or less level region, and then a second abrupt drop at about 250°C. Dacron is a two-phase system; it is partially crystalline, partially amorphous. Acetate rayon is a one-phase system; it is entirely amorphous. The two drop-offs in stiffness of Dacron correspond to the melting of the two phases. The drop-off at 250°C arises from the melting of the crystallites; the drop-off in the region of 60°C to 100°C corresponds to the "melting" of the

[3] Du Pont polyester fiber.

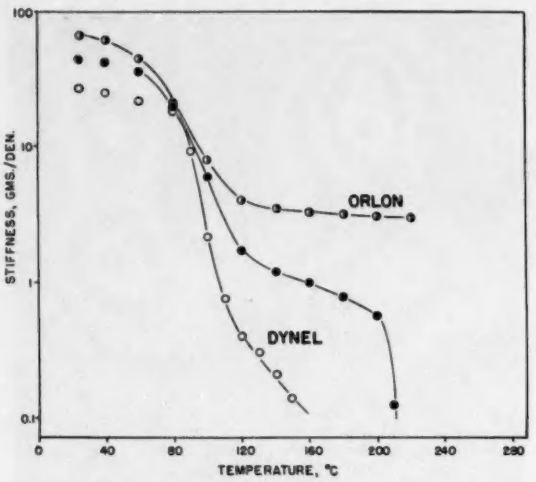

Fig. 7. Stiffness-temperature behaviors of Orlon, Dynel, and an experimental acrylic fiber.

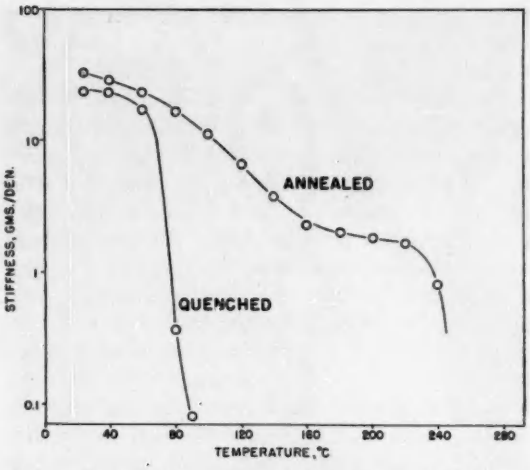

Fig. 8. Stiffness-temperature behaviors of quenched and annealed polyethylene terephthalate.

amorphous phase. The second-order transition temperature of Dacron is about 80°C. The drop in stiffness of acetate rayon in the region 160°C to 200°C is due to the "melting" of the amorphous phase since this polymer is entirely amorphous.

These facts enable the development of a more basic definition of the second-order transition temperature. It is the melting point of the amorphous phase of the polymer.[4]

Below the second-order transition temperature of a polymer the system is a frozen mass. The polymer chains and their segments are relatively immobile, and the system exhibits a high resistance to deformation, i.e., a high stiffness. Above the second-order transition temperature the chain segments that are in the amorphous phase are freely mobile. If the system is entirely amorphous, the system will be freely mobile above the second-order transition temperature and will be a viscous liquid. If the system is partially crystalline, only the segments in the amorphous phase will be mobile; those in the crystallites will still be immobile and will exert a reinforcing action resulting in a system stiffness intermediate to that of the viscous liquid and of the frozen mass. The partially crystalline polymer system will not become a viscous liquid until the first-order transition temperature, the melting point of the crystallites, is exceeded.

Since the second-order transition temperature is a property of the amorphous phase the effects associated with it, in this case a drop in stiffness, should be the more pronounced the greater the concentration of the amorphous phase and the less crystalline the system. This is illustrated in Figure 7, which shows the stiffness-temperature curves of three acrylic fibers. The most crystalline fiber, Orlon (polyacrylonitrile),[5] shows that least drop-off in stiffness at the second-order transition temperature. The least crystalline fiber, Dynel (copolymer of vinyl chloride and acrylonitrile), shows the greatest drop-off. An experimental fiber of intermediate crystallinity, as judged from the X-ray diffraction patterns, shows an intermediate drop-off in stiffness.

Figure 8 also shows the more pronounced drop-off in stiffness by the more amorphous system. Here two fibers were made from the same polymer, polyethylene terephthalate. One was carefully annealed to allow as complete a crystallization as possible. The other was quenched from the melt in order to minimize the crystallinity. The more pronounced

[4] It is perhaps incorrect to use the term "melt" in reference to amorphous materials. It implies a more abrupt and definite change than is observed. On the other hand, the term "soften" is judged to be too vague and gradual to adequately describe the change. The change that occurs is that of a glass melting, and it is probably more correct to call the second-order transition temperature the glassy-state transition temperature. In the text the term "second-order transition temperature" is used in recognition of its more popular usage, and the term "melt," in reference to the amorphous phase, is used for convenience.

[5] Du Pont acrylic fiber.

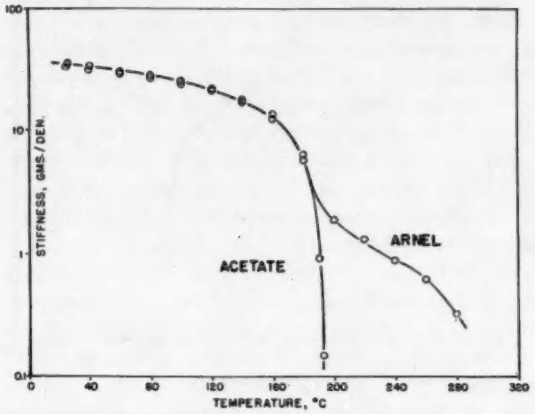

Fig. 9. Stiffness-temperature behaviors of Arnel and acetate rayon.

drop-off in stiffness of the quenched more amorphous fiber is easily seen.

Two other illustrations of the relation between second-order transition temperature drop-off in stiffness and amorphous content are given in Figures 9 and 10. Figure 9 compares the behavior of acetate rayon and the crystalline cellulose triacetate fiber, Arnel. Below the second-order transition temperature, 180°C, the fibers are essentially identical in stiffness-temperature behavior. Above it, the crystallites in Arnel maintain the stiffness at an intermediate level, while the absence of crystallites in acetate results in a viscous liquid. Arnel does not become a viscous liquid until its crystallites are melted at 290°C.

Figure 10 compares the behavior of nylon (polyhexamethyleneadipamide) and Dacron. The second-order transition temperature of nylon is about 45°C. At room temperature nylon is close to this so its stiffness is already in the lowering stage. At room temperature Dacron is still well below its second-order transition temperature of 80°C, so it is still stiff. At about 140°C, above the transition temperature of both, nylon is stiffer than Dacron, presumably because it is more crystalline.

Figure 11 shows the stiffness-temperature behavior of viscose rayon, Acrilan (polyacrylonitrile), and Saran (vinylchloride, vinylidene chloride copolymer). Saran exhibits a stiffness drop-off at 0°C, its second-order transition temperature. Acrilan, in its behavior, is essentially the same as Orlon. Viscose rayon, when dry, as in these tests, does not exhibit a second-order transition temperature in the range studied (up to 300°C). It is likely that the molecules decompose chemically before the amorphous phase melts. Somewhat cruder measurements on cotton and wool resulted in the same interpretation for these materials.

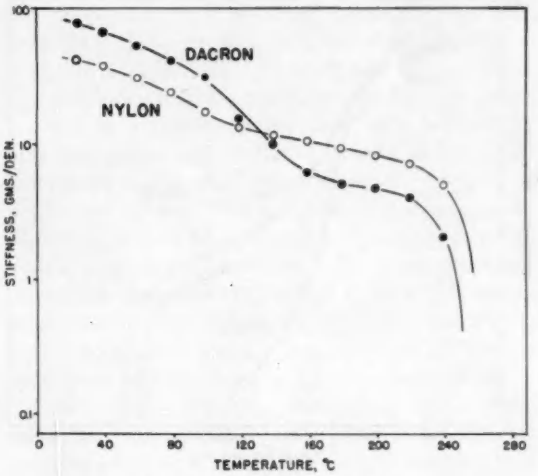

Fig. 10. Stiffness-temperature behaviors of nylon and Dacron.

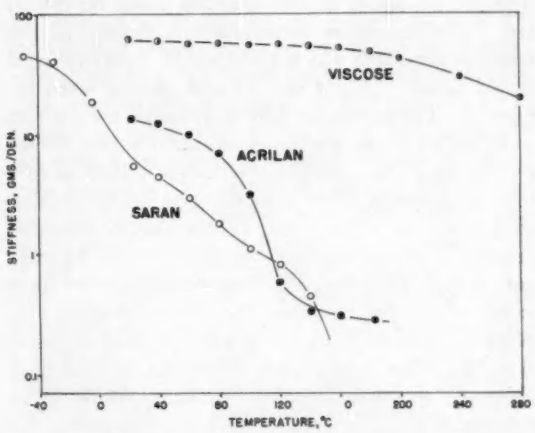

Fig. 11. Stiffness-temperature behaviors of viscose, Saran, and Acrilan.

Figure 12 illustrates a practical application of this work. It shows the stiffness-temperature curves of several acrylic fibers, and marked on each are the minimum and maximum dry-ironing temperatures of fabrics made from the fibers. The minimum dry-ironing temperature is defined as the minimum tem-

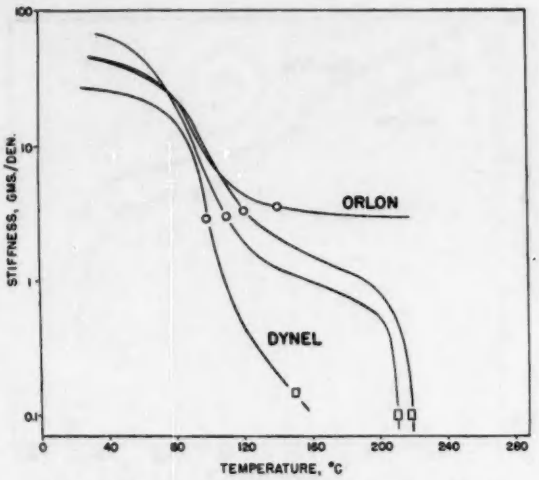

Fig. 12. Stiffness-temperature behavior and dry-ironing temperatures.

perature at which mussy wrinkles could be ironed out. The maximum temperature is defined as the temperature above which a noticeable change in hand would occur. (Color change and glazing were ignored.) The particular fabrics available for the test were rather heavy and compact, not the best choice for the test. Nonetheless, the results indicate a correlation between fiber stiffness and fabric ironing characteristics. The fiber, in the fabric, must be heated to a sufficiently high temperature that its stiffness falls to a certain value low enough for the fiber to be readily deformed and the fabric flattened out. With the present fabrics this stiffness level is about 3 g/den. The temperature necessary is somewhat above the second-order transition temperature of the polymer system comprising the fiber. Similarly, the fibers must not be heated to such a temperature that their stiffness falls below a critical value, 0.1 g/den, else permanent damage to the hand of the fabric results. It is likely that a similar correlation would occur between fiber stiffness and the glazing temperature of the fabric. However, softer fabrics than those used here would be required to demonstate this.

Resiliency-Temperature Behavior

The recovery of a fiber from a stretch is a function of time. Generally it is found that after the removal of the stretching force the fiber immediately recovers a portion of the stretch, and then continues to recover more and more but at a slower and slower

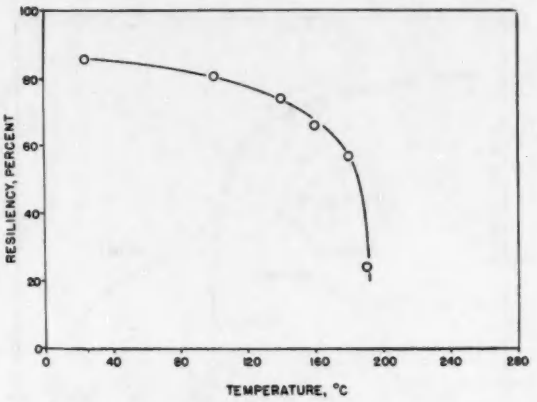

Fig. 13. Resiliency-temperature behavior of acetate rayon.

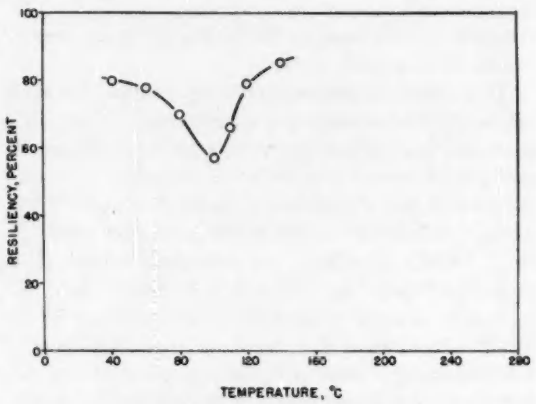

Fig. 14. Resiliency-temperature behavior of Dynel.

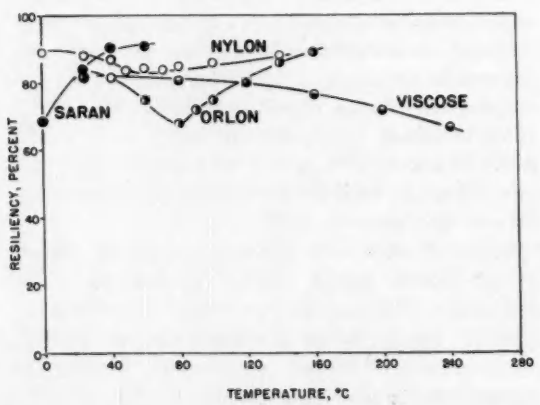

Fig. 15. Resiliency-temperature behavior of different fibers.

rate. The complete picture of the resiliency, or recoverability, of a fiber would require measurements like those used in creep recovery. The particular arbitrary definition of resiliency used here, and derived from Figure 4, was chosen because it is easily calculable, is readily measured along with the stiffness in the technique used, and is probably as significant as any other short-time measure of resiliency.

Figure 13 shows the resiliency-temperature behavior of acetate rayon. The resiliency is seen to decrease slowly at first and then more rapidly as the second-order transition temperature is reached. Cellulose acetate is a thermoplastic, and one would expect it to get "deader" as the temperature is increased.

Figure 14 shows the resiliency-temperature behavior of Dynel. It shows the same decrease in resiliency on heating up to the second-order transition temperature. However, the crystallites in Dynel prevent it from becoming a liquid above this temperature, and the resiliency is found to increase on further heating, yielding a minimum in resiliency at the second-order transition temperature.

This behavior is general, as shown in Figure 15. Each fiber exhibits a minimum in resiliency at the second-order transition temperature. Also, it can be noted that the magnitude of the effect, the depth of the minimum, is greater, the higher the amorphous-phase content of the polymer. This shows, as was the case with the drop-off in stiffness, that the second-order transition temperature is an amorphous-phase property.

Another aspect of resiliency on which some measurements were made is the ability of the fiber to maintain its tautness when it is stretched and held at a given stretch. The decrease in tautness with time is termed stress decay. A limited number of measurements on the fibers showed that the rate of stress decay is at a maximum at the second-order transition temperature.

As might be inferred from the recovery behavior of the fibers, and as was indeed seen in the load-elongation diagrams, the curvature in the initial portions of the stress-strain curve is a maximum at the second-order transition temperature.

Thus resiliency, as evidenced by recovery from stretch, rate of stress decay, and curvature in the stress-strain curve, is at a minimum at the second-order transition temperature. By defining the second-order transition temperature as the melting point of the amorphous phase of the polymer, it was easy to explain the drop-off in stiffness at this temperature. However, this definition does not offer a ready explanation for the minimum in resiliency. The explanation of this minimum requires the use of a rather basic concept of the viscoelastic behavior of polymers and results in the most basic definition of second-order transition temperature.

The amorphous phase of the polymer can be likened to a mass of spaghetti in which there exists a wide range of configurations. There are short sections of chains, segments, that are essentially straight; others form short rather sharp bends; and others form long gradual bends. Also, there are all sorts of gradations of these three types of configurations.

Consider the intrinsic mechanical behavior of these different types of configuration by seeing what happens when each, as a single unit, is acted on by a directed tensional force. There are two types of behavior shown by the straight segments. Those segments which are parallel with the direction of the applied force respond by stretching, and this stretch is afforded by the stretching of the primary valence bonds of the backbone of the segment or by the distortion of the primary valence angles. Compared with other mechanisms which afford segment response, these primary valence stretches or distortions require the application of relatively high forces; they are very stiff mechanisms. The straight segments which happen to be inclined to the direction of the applied force respond by swinging into line with it. This response is afforded partly by the stretching of primary valence bonds and opening up of primary valence angles and partly by rotation of these bonds. Rotation about bonds, which is like a swiveling, requires much less force than stretching bonds. Thus the response of the inclined straight segments to the applied force is much less stiff than that of the parallel segments. The bends in the segments respond by straightening out, much like the crimp in fibers. This straightening out is afforded, likewise, by the rotation, or swiveling, of the segment about the primary bonds. The response of the bent segments is thus also less stiff than that of the parallel straight ones. The long gradual bends can afford a given magnitude of response by swiveling about fewer bonds than the same length of segment composed of a number of sharp bends. Thus the longer and more gradual the bend, the less stiff it is. This can be compared with high and low frequency crimp in fibers.

Thus the distribution of configurations results in

a distribution of intrinsic resistance to deformation, that is, of stiffness. This is the intrinsic behavior, though, and it is modified when all the segments are collected together in the mass. The response of the straight segments which are parallel with the applied force is not affected by the presence of neighboring segments. However, the inclined segments, the sharp bends, and the gradual bends are affected, in their response, by the presence of neighboring segments. This effect arises because for these segments to swing into line or to straighten out requires that neighboring segments must be moved out of the way. The primary result of this moving of neighboring segments is that it takes time, and the greater the number of neighboring segments that have to be moved, the greater the amount of time required. The longer and more gradual the bend that is to be straightened out, the greater the number of neighboring segments which have to be moved. Thus this type of deformation mechanism requires the greatest amount of time. Sharper bends move fewer segments when they straighten out; thus this type of deformation requires less time. The true stretching of straight segments requires that essentially no neighboring segments need be moved; thus this mechanism requires essentially no time for its operation.

Thus the distribution of configurations yields a distribution of deformation mechanisms which exhibit a wide range of intrinsic stiffnesses and also a wide range of the time necessary for the response of these mechanisms. This latter is the distribution of relaxation times, a basic concept of the viscoelastic theories of polymers.

It is interesting to note that the particular mechanisms which exhibit the greatest stiffness in their response also exhibit the shortest time necessary for that response and that the mechanisms which are the softest are also the slowest.

If one could analyze the amorphous phase and count the different types of configuration, measure (or calculate) the times necessary for their response, and then plot the results, one would get a distribution curve. A guess as to what such a curve could be like is given in Figure 16. The most important features of the curve are that it exhibits a maximum and that the times involved extend over many powers of ten.

Whether one is conscious of it or not, time is operating as a variable in everything that is done with high polymers. Measurements are made in a fixed

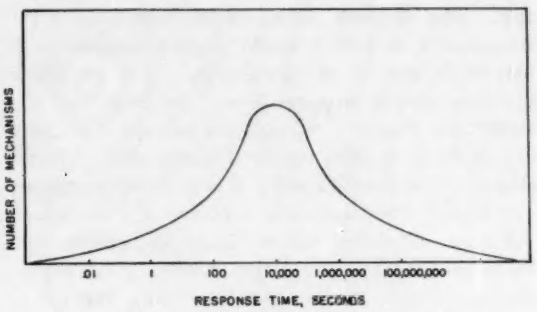

Fig. 16. Idealized conception of distribution of relaxation times.

time interval, or sometimes a fixed time schedule is followed. The interval or schedule is sometimes deliberately set with certain fundamental considerations in mind. More often, however, the interval or schedule is set consciously or unconsciously by limitations of the equipment used or of the operator, or by the patience or lack of it of the operator. Whatever the cause, time is operating, and it is just as important, and as integral a part of the picture, as stress or strain. Time operates as a variable in the force-response behavior of high polymers as follows: In general, a force is applied to the system and the system as a whole exhibits a deformation, say, a stretch. The applied force is distributed over the different segments, and each attempts to respond to its share of the force. In some time after the first application of the force the situation inside the system is as follows: Each mechanism of deformation whose response time is shorter than this reference time will have achieved the response that is in equilibrium with the force on it. Mechanisms whose response times are greater than this reference time, due to the internal viscosity effect arising from moving neighboring segments, will be delayed such that only a portion of this equilibrium deformation is achieved in this reference time. During any time interval after this reference time, the continuation to completion of the response of these slower mechanisms may be seen by the operator. He might see them operate as a creep of his sample under a constant applied load or as a decay of load at a constant extension. If he is making stress-strain measurements these delayed responses will always lag behind the application of stress. The lag is in time; however, since stress-strain measurements involve either a constant rate of loading or of extension, the lag appears to be in load or extension. In either case the

lag results in a curvature of the stress-strain curve. If the operator is measuring recoveries from stretch, the lag is operating both coming and going. He might not be aware of the lag during the loading cycle, but the lag is very evident during unloading because the operator knows what the equilibrium unloaded state should be. It should be the same length as his original sample length. Instead he notices a loading-unloading cycle which shows hysteresis and an apparently permanent set in length on returning to zero load. The hysteresis and set are due to the lagging behind the load of these delayed mechanisms during the loading and unloading cycles. In practice the operator is concerned with two reference times, not one. One reference time is very short and is determined by either his, or his instrument's, perception; perhaps of the order of one second. The other is relatively long, perhaps of the order of a minute or an hour, and is determined by how much time the operator wishes to spend on the measurement, i.e., by his patience. The general delay of response, though, is taking place over *all* intervals of time. The operator, however, lumps all mechanisms whose time delays are less than his perception limit into one group (terms them "instantaneous"), ignores as nonexistent those mechanisms whose time delays are greater than his limit of patience, and is concerned with those in between. Those intermediate mechanisms he can see operate as time dependencies in his measurement.

Let us return to the distribution of response times curve and locate on it at a time schedule set by such perception and patience limits, say 1/5 sec and 1 sec. This time slice lies between the limits of A and B on the idealized distribution curve, Figure 17. All the mechanisms to the left of A will have deformed, in response to the applied force, faster than the operator could see them. The mechanisms to the right of B will have only partly responded by the time the operator loses interest (also, they will have responded to decreasingly small amounts). The mechanisms between A and B will be responding to completion while the operator is watching and will be seen by him as time-dependent responses.

As illustrated in Figure 17, the number of "instantaneous" mechanisms is a small fraction of the total; these are the stiffest mechanisms. The number that the operator sees respond is also a small fraction, while the number that he doesn't wait for is a large fraction. This means that the response of the system to the applied force will be that of a stiff material and that, since there are only a few mechanisms that respond between the two reference times, there will be only small evidence of a time effect on the response—the system will exhibit little creep and little stress decay; the stress-strain curve will exhibit only a little curvature; and recovery from stretch will be high.

If the operator worked on another time schedule such that he considered as instantaneous all responses that occurred in less than a day, that he ignored as too slow those which occurred in more than a week and that he observed those which occurred in the intervening days, his time schedule would be placed between the limits A and B in Figure 18. Now the mechanisms faster than the reference "instantaneous" time, those to the left of A, represent a considerable fraction of the total number of mechanisms, and they include a great number of the easily deformable ones. Thus the "instantaneous" response of the system will be that of a very soft material. It will exhibit low stiffness. The fraction of the mechanisms whose response the operator sees during his week's vigil is again a small fraction of the total, so that little additional response will be noted. The fraction ig-

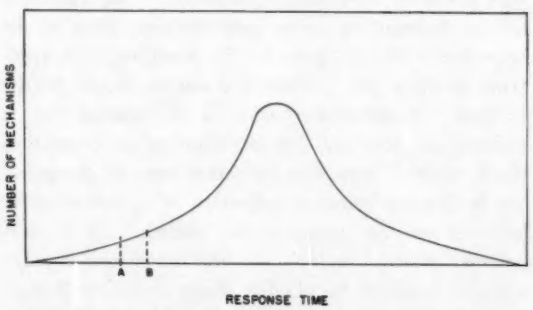

Fig. 17. A 0.2 to 1.0 sec time slice on an idealized distribution curve.

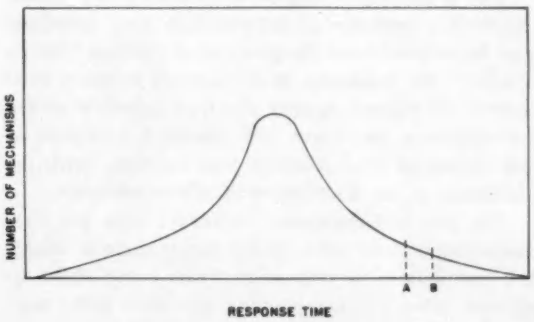

Fig. 18. A 1 to 7 day time slice on an idealized distribution curve.

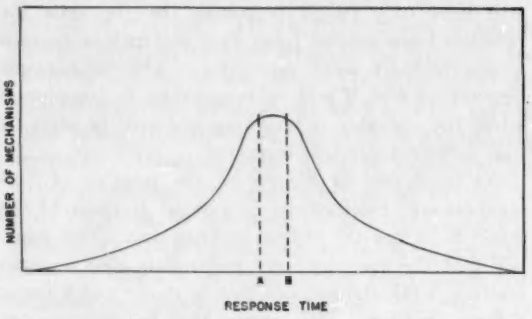

Fig. 19. A 1 to 5 minute time slice on an idealized distribution curve.

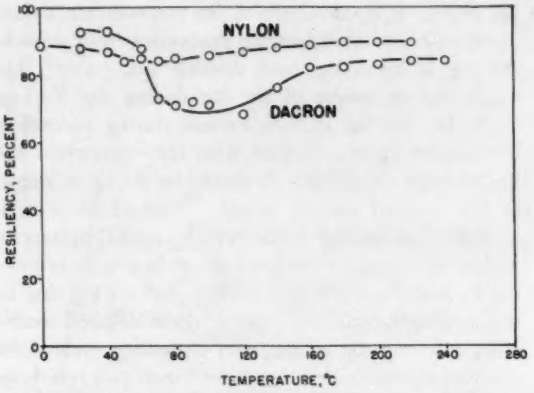

Fig. 20. Resiliency-temperature behaviors of nylon and Dacron.

nored is a small fraction of the whole. The operator would characterize the system as a very soft material and state that it exhibited very little creep or stress decay, gave an essentially straight stress-strain curve, and exhibited good recovery from stretch.

If now an intermediate time scale is adopted wherein no observations are made for 1 min after the start of the test, nor after 5 min, but are made between these limits, the time schedule occurs between *A* and *B* in Figure 19. The mechanisms which are ignored as being too fast to measure are intermediate to the two previous cases. This means that the stiffness exhibited by the system is between the high value for the second observations and the low value for the week observations. The number of the mechanisms which respond during the time of observation is *greater*, however, than in either of the previous time schedules. The observed time dependence of the response will thus be greater than in the other time schedules. The system, now, would be described as being of intermediate stiffness, exhibiting pronounced creep, stress decay, and curvature in the stress-strain curve, and poor recovery from stretch.

The stiffness and magnitude of the apparent time-dependent response at intermediate time schedules can be inferred from the previous discussion. Specifically, if the resiliency, in the form of recovery from stretch, is plotted against the time schedule of the measurement, the curve will exhibit a minimum at the particular time schedule that coincides with the maximum in the distribution of relaxation times.

The previous discussion concerned only the constant temperature case. If the temperature is raised, the distribution of relaxation times curve shifts to shorter times. Accompanying this shift there may be a change in shape of the curve; however, it is most likely that it maintains its two principal features of a maximum and a wide range of time. Therefore, if the operator adopts a convenient time schedule for all his measurement, say the 1/5 to 1 sec schedule given as an example in Figure 17, and progressively raises the temperature of the measurement, the distribution of relaxation times curve will sweep past his chosen slice of time. The number of mechanisms whose response may be noted in this slice will be small at some low temperature but will increase with increasing temperature to some maximum value and then decrease again with further increase in temperature. This is the origin of the minimum in resiliency. The temperature at which it occurs is the second-order transition temperature, which may thus be rather basically defined as that particular temperature at which the maximum in the distribution of relaxation times coincides with the time schedule of the experiment.

In addition to the explanation for the existence of the resiliency minimum, the foregoing discussion offers a rather interesting possibility. The sweeping of the distribution curve past the time slice of the experiment is analogous to the scanning of a spectrum with a slit. Thus the entire shape of the resiliency-temperature curve is of interest for it reflects the form of the distribution of relaxation times curve. True, this reflection may be distorted, but it is nonetheless a reflection of a rather basic behavior of the high-polymer system. In certain polymer systems such as plasticized systems, copolymers, or polymer blends, the shape of the resiliency-temperature curve offers considerable useful infor-

mation, since in such systems the distribution of relaxation times is subject to considerable modification and distortion. The particular polymers that are used to make synthetic fibers are mostly quite crystalline and in some ways uncomplicated, and the shape of the resiliency-temperature curve is not particularly informative. However, Figure 20 illustrates one application of the shape of the resiliency-temperature curves of textile materials. It compares the behavior of nylon and Dacron. Both are normal in that each exhibits a minimum at its second-order transition temperature. They differ in that the resiliency of nylon rather quickly increases again as the second-order transition temperature is exceeded, while that of Dacron remains at relatively low values for a relatively long temperature interval above its second-order transition temperature. From a structural point of view, this means that the amorphous phase of nylon consists of segments which have a normal distribution of configuration and relaxation times, while the amorphous phase of Dacron has relatively broader distributions. The Dacron distributions are broader at the long-time end. This would result from the presence of structural elements which are functionally like crystallites but much smaller. From a practical point of view these broadened distributions result in the maintenance of low resiliency through an important temperature range, that of a tire cord in use, 100° to 140°C. Nylon is quite resilient at this temperature; Dacron is not; and it is generally known that Dacron has been disappointing in its application as tire cord for passenger tires. From the foregoing discussion it would appear that Dacron would be improved for tire-cord application if the long-time end of its distribution of relaxation times curve could be minimized. This would be best done by removing the small pseudocrystallites from the amorphous phase by changing them into real crystallites, that is, by a rather complete annealing treatment of the fiber.

Acknowledgment

It is a pleasure to acknowledge the help of Mr. R. C. Gross, who obtained most of the experimental results reported here.

References

No particular literature reference has been cited in the text, though many have been used in establishing the general background. The following very short list of publications is offered for suggested reading, either because of their general treatment or because they are representative of the different aspects or interpretations of second-order transition temperature phenomena.

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A Study of Blended Woolen Structures

Part II: Blend Distribution in Some Wool-Nylon and Wool-Viscose Yarns[1]

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Introduction

In Part I [5] some statistical aspects of the problem of blend uniformity were discussed. It was pointed out that perfect blend uniformity is unattainable on machinery which merely shuffles fibers together in a random fashion. Specific statistical criteria for the ideal random yarn as well as methods of evaluating the degree of blend inhomogeneity in real yarns were developed. The present report provides some experimental data on the distribution of blend in a series of woolen wool-nylon and wool-viscose yarns.

It is commonly recognized that yarns spun from a blend of fibers do actually exhibit imperfect blend distribution. It is also generally appreciated that the behavior of a blended fabric may depend to a considerable extent on the type and degree of inhomogeneous mixing of the component fibers. Perhaps the most obvious example of this effect occurs as irregular dyeing when there is undue aggregation of one type of fiber. There are, besides visual consequences of this condition, a number of other fabric characteristics which are often associated with it.

Frequently the "handle" of a blended fabric is said to depend on the tendency of a particular fiber type to spin to the outside of the yarn. Dimensional stability [2], abrasion resistance [1], milling behavior [13], and efficiency of napping [12] are several other characteristics of blended fabrics that have been related directly or otherwise to the manner in which the different component fibers of a mixture are mingled together.

A direct experimental method of determining the distribution of fibers in a blended yarn might be expected to shed some light on many of these problems. Recently Macormac and Reed [8] made a study of some wool-rayon and wool-nylon fabrics by chemical and microscopic methods. Lund [7] presents some experimental data on the distribution of black and white fibers in viscose fabrics, as well as information on blends of viscose with other fibers. Hampson and Onions [4] more recently gave some data on wool rovings containing black and white fibers.

It is a principal object of the work encompassed by this report and Part I to develop experimental and statistical techniques for characterizing quantitatively and more completely than previous methods the types and extent of blend inhomogeneity in any yarn. A pedigreed series of wool-nylon and wool-viscose woolen yarns, prepared for a continuing experimental program, are analyzed by the methods developed. The techniques are considered to be of general applicability. The specific findings on the particular yarns that were studied probably should not be generalized without caution. They, obviously, pertain to woolen-type yarns spun with the kind of fibers that were used and under the spinning conditions that obtained.

On the other hand, this may be only a broad limitation on the usefulness of the data.[2] The woolen spinning systems are relatively simple, and the particular processes employed in the present case were standard. The fiber stocks employed were also commercially standard. Therefore, while not representative of all possible commercial types, the yarns that were studied are felt to be typical woolen yarns.

The Questions To Be Answered

Consider that a yarn resembles an extremely attenuated cylinder. The spatial location of any fiber may, at first, be described in terms of its position

[1] Part of a research program conducted at Fabric Research Laboratories, Inc., with the support of the United States Navy, Office of Naval Research, and Bureau of Supplies and Accounts. Portions of the experimental data and the techniques developed herein form part of the M.S. thesis of M. G. Bloch, Textile Division, Massachusetts Institute of Technology, June, 1954. Presented in part before the Fiber Society, May, 1954, Charlottesville, Virginia.

[2] Recent private communications indicate that many characteristics of blend distribution found for the subject woolen yarns have also been observed in worsted yarns spun on pin-drafter and gill-box equipment.

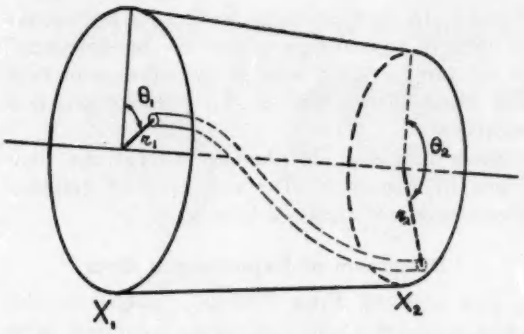

Fig 1. Diagrammatic view of yarn as a cylinder showing the location of a single fiber at two cross-sections.

within the cylinder. Its center, say, is at X and its ends are at $\pm \Delta X$. In the cross-section of the yarn at position X, the center of the fiber occupies a position displaced from the axis of the yarn, which may be described by a radial distance, r. On the circle with radius r, the center may be considered to be displaced θ from an arbitrary vertical (see Figure 1).

Beyond locating a section of a fiber in terms of X, r, and θ in the yarn the description of fiber position becomes extremely complex. At some point along its length the fiber may appear at the surface of the yarn, and elsewhere it may be found in the "heart" of the yarn. Frequently, there may be fibers which, because they are curled or hooked [10, 11], return on themselves and cross a given cross-section twice or more. The crimp of the fiber contributes to the complexity of its path, and superimposed on the whole is a semi-uniform helical distortion due to yarn twist.

Therefore, the paths of individual fibers for all of their lengths are not amenable to precise analytical descriptions. It will not be possible by any of the methods developed herein to ascertain whether or not a fiber whose center is at X, r, θ appears elsewhere at $X + \Delta X$, $r + \Delta r$, and $\theta + \Delta\theta$. On the other hand, each location of the *yarn* may be described by the same coordinates X, r, and θ, and the occurrence of some part of a fiber at such points may be noted.

In the present problem the experimental procedure entails sectioning the yarn at regular intervals, say at X_1, X_2, etc. Each section is divided into concentric rings of radii r_1, r_2, etc. Each section also is divided rotationally into octants, starting with an arbitrary vertical. The number and kind (whether nylon, wool, or viscose) of fibers occupying each ring and octant at each section are determined.

While nothing can be said about the path of any particular fiber in the yarn by this method, the distribution of the blend components along the yarn and within yarn cross-sections can be ascertained. Thus, the blend composition of the yarn and its variability can be described in three dimensions: longitudinally, radially, and rotationally.

It is presumed, in this analysis, that yarn cross-sections contain random assortments of fiber ends, middles, etc. It is also assumed that the instantaneous denier of any fiber at a cross-section is a random variable uncorrelated with the total number of fibers or the particular concentration of blend at that section. This appears reasonable in view of Monfort's [9] finding for worsted yarns that there was no correlation between the number of fibers in a cross-section and the mean-diameter arithmetic mean of these fibers.

Now, with data at hand of the sort just described, questions of the following kind are to be answered:

1. What is the longitudinal blend distribution in a given yarn? How, if at all, does the distribution differ from what would be predicted on the basis of statistical criteria? [5] Is there a correlation between total denier at a section and blend composition? Is the linear blend distribution affected by twist? How does the Index of Blend Irregularity [5] vary with blend composition?

Some models of longitudinal distribution of both

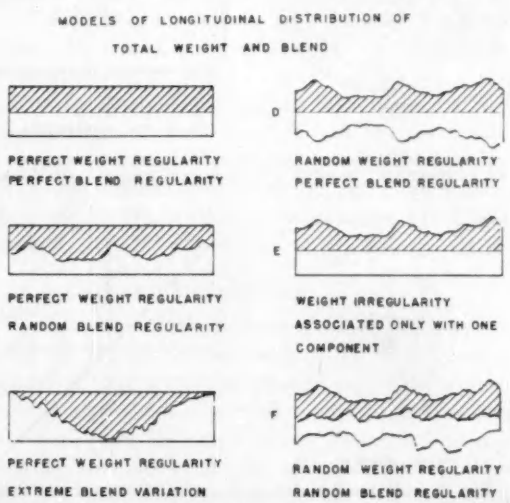

Fig. 2. Diagrammatic description of various combinations of weight and blend irregularity along a yarn.

total number and proportions of two kinds of fiber are given in Figure 2. The several individual representations are selfexplanatory. It is a foregone conclusion that the perfectly uniform weight-blend situations as depicted by Figure 2*a*, *b*, and *c* are unrealistic.

Some of the other conditions, however, are not to be immediately discarded. For example, is there a tendency for thick spots to be predominantly of one type of fiber, as illustrated by Figure 2*e*? If this were so, a plot of blend proportion vs. total section weight would indicate such a trend—the greater the total denier of a section, the higher the per cent concentration of one type of fiber. This and other types of conditions are treated below.

2. What is the pattern of radial blend distribution? For example, is there a tendency for a particular fiber type to spin to the surface of the yarn? What are the effects of twist and average blend composition on radial distributions?

Pictorial and graphical representations of several kinds of possible radial blend distribution patterns are given in Figure 3. The graphical representation requires considerable comment and is discussed later.

3. What is the pattern of rotational blend distribution? Is there evidence of excessive aggregation of fibers of a given type to produce "one-sidedness" in the yarn? Again, what is the influence of twist and blend composition on this phenomenon, if it occurs?

Some rotational distribution patterns are illustrated by Figure 4. The two kinds of graphical presentation are discussed later.

Discussion of Experimental Data

Two series of 3-run (900-den) woolen blended yarns, wool-nylon, and wool-viscose were spun using 12 months 64's Texas wool, 3-den 2½-in. crimped nylon staple, and 3-den 2½-in. viscose. The average deniers of the fiber stocks found by sampling from roping were 4.32 for the wool, 3.35 for the nylon, and 3.07 for the viscose. The entire series of yarns included blends of 12.5%, 25%, 50%, and 75% by weight of the nonwool fiber. All blends were spun to nominal twists of 4½, 7, 9½, 12, and 14½ t.p.i. Selfblends of 100% wool, 100% nylon, and 100% viscose were also spun in all twists. For the study of blend distribution all of the wool-nylon yarns in the low (4½ t.p.i.), medium (9½ t.p.i.), and high (14½ t.p.i.) twist were examined, the same twists

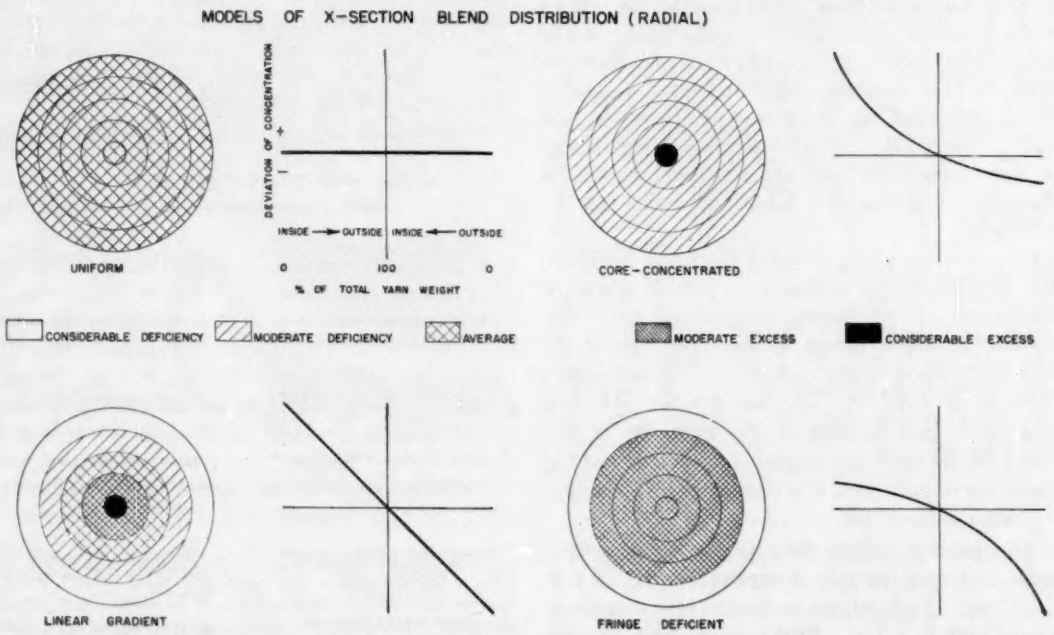

Fig. 3. Idealized depiction of radial-blend patterns showing how each pattern would be represented by an integrated "inside-outside" curve.

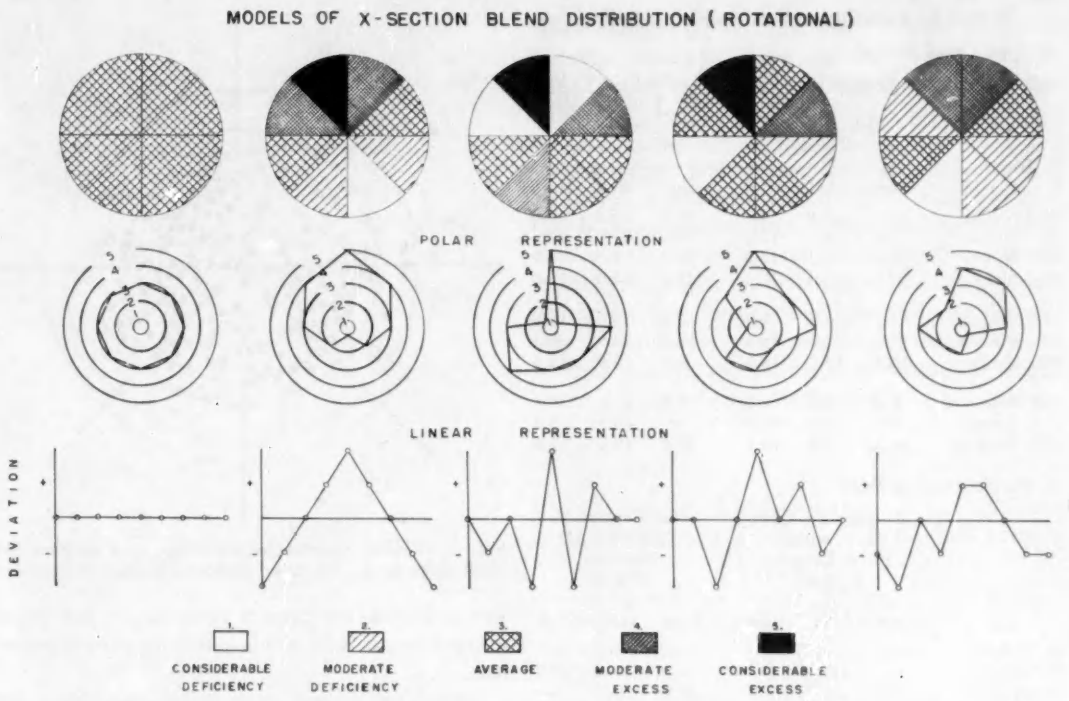

Fig. 4. Idealized depiction of rotational-blend patterns showing how each pattern could be represented on polar or linear coordinates.

in all but the 75% viscose yarns, and the same three twists for the selfblend yarns.

Yarn samples were cemented without tension across small cardboard frames, taking care not to disturb the original twist. The frames were inserted in large gelatin capsules which were then filled with a polymerizing mixture of methyl methacrylate, plasticizer, and catalyst and capped. Polymerization was carried out at 130–140°F for 24 hr or until the mixture had hardened satisfactorily for cutting. For good background contrast, Sudan Red III was added to some of the prepolymerized embedding mixtures. The methacrylate matrix was eventually embedded in Tissumat prior to sectioning with a sliding microtome. It was necessary to get sections about 5μ thick for clear images. To develop better separation, various textile stains were applied to the face of the embedment prior to sectioning. The thin sections were then mounted for microprojection at a net magnification of 175×.

Cross-sections were taken every 2 in. (5 sections) within five different 10-in. lengths of yarn. The 10-in. lengths were selected at distances of several yards. Therefore, at least 25 sections were taken in all for each yarn.

Data for analysis of longitudinal, radial, and rotational characteristics were all collected simultaneously from microprojection images typified by Figure 5. For convenience, however, the three dimensions will be discussed separately, in the order just listed.

A. Longitudinal Characteristics

There are several instruments available for the rapid and precise measurement of yarn weight regularity over long-sample lengths of yarn. The tedious method employed in this work of cutting sections and counting fibers is by no means recommended for getting a measure of simple weight variability. Besides the usual thickness measurement devices, even capacitance [6] measuring instruments are reported

TABLE I. Variability of Total Denier per Section

A. Fiber Count Method

Blend (%)	Average Per Cent C. V. within 10-In. Lengths (Twist)			Per Cent C. V. Total for All Sections (Twist)		
	Low	Med.	High	Low	Med.	High
12.5 Nylon	11.1	13.8	14.3	11.0	15.4	15.0
25 Nylon	11.0	14.4	13.1	12.0	17.9	15.6
50 Nylon	11.3	10.2	17.0	12.6	9.6	18.9
75 Nylon	11.8	16.5	15.7	18.0	16.0	19.6
12.5 Viscose	14.7	10.7	9.9	17.6	13.0	11.0
25 Viscose	17.3	11.2	16.4	22.0	13.0	20.3
50 Viscose	16.6	13.1	14.6	22.1	15.0	15.4
100 Wool	6.5	20.4	12.4	6.9	14.2	10.7
100 Nylon	—	15.0	10.5	—	18.5	9.4
100 Viscose	14.5	13.8	13.1	12.2	19.9	17.6

B. Pacific Evenness Tester

Blend (%)	Average Per Cent C. V. within 10-In. Lengths (Twist)			Per Cent C. V. Total for All Sestions (Twist)		
	Low	Med.	High	Low	Med.	High
25 Nylon	—	—	—	—	—	14.2
50 Nylon	—	—	—	—	—	17.7
75 Nylon	—	—	—	20.5	21.5	—

T about 200–250 for all yarns.

From Part I, by equation 3, CV_T would equal $100/\sqrt{200} = 7\%$.

From Part I, by equation 2 CV_T would equal $100/\sqrt{400} = 5\%$.

to be satisfactory for measuring the overall weight irregularity of blended yarns.

Information on total weight irregularity was obtained in the present work as a part of collecting the blend-distribution information. As a gross check on this data, several yarns were tested on a mechanical compression-type uniformity tester (the Pacific Evenness Tester). This information is given in Table I, and, also, Figure 6*a*, *b*, and *c* illustrates graphically the variation in total denier, both within 10-in. lengths and overall for the 25 sections examined for three different yarns. The numerical data of Table I confirm the impression that almost the entire variation in weight, other than long-period fluctuations in yarn number, is experienced between sections about a fiber length apart within 10-in. specimens. The data also indicate the very common situation that total yarn irregularity exceeds the theoretical values that one might calculate by use of the equations for the ideal yarn. However, as

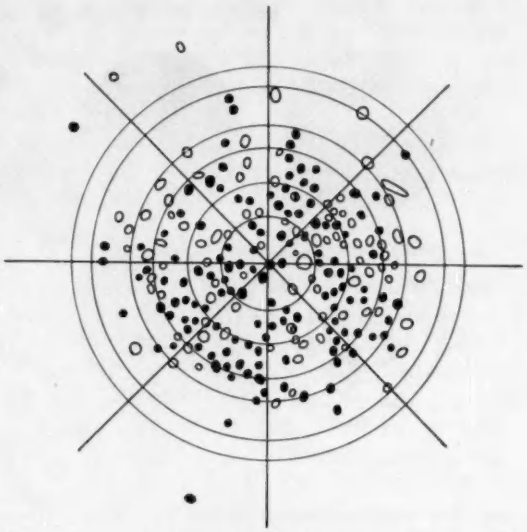

Fig. 5. Typical microprojection image of a medium twist 50% nylon yarn. Darkened sections represent nylon fibers.

just indicated, the present methods are not recommended for analysis of this particular yarn characteristic.

Figure 6*a*, *b*, and *c*, however, provides a preliminary impression of the extent of variation of blend by showing the fluctuation of each fiber component from section to section. The actual variation in blend composition is given in Table II for the entire group of yarns examined, and illustrated graphically in Figure 7*a*, *b*, and *c*.

One matter of interest in both Tables I and II should be mentioned. It will be observed that total C. V. for a given yarn is sometimes less than the average C. V. within 10-in. lengths. The C. V. values were all approximated by the mean-range

TABLE II. Variability of Per Cent Weight of Nonwool Fiber per Section

Blend (%)	Average Per Cent C. V. within 10-In. Lengths (Twist)			Per Cent Total C. V. for 25 Sections (Twist)		
	Low	Med.	High	Low	Med.	High
12.5 Nylon	21.5	26.7	29.6	22.2	28.7	25.9
25 Nylon	18.0	18.6	20.7	18.6	20.5	19.1
50 Nylon	12.7	10.9	10.2	11.6	13.0	11.4
75 Nylon	7.4	6.2	7.3	6.7	6.8	6.7
12.5 Viscose	28.0	21.6	24.1	25.0	19.4	26.1
25 Viscose	17.4	22.1	24.2	17.0	20.0	22.4
50 Viscose	12.4	11.0	9.5	12.0	13.0	9.0

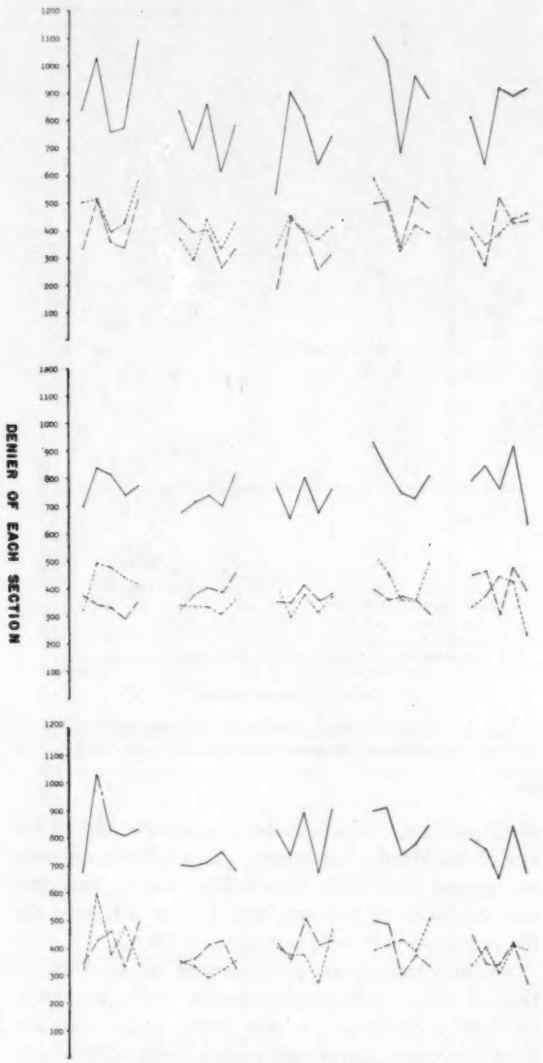

Fig. 6. Total denier and denier of components in each of 5 cross-sections taken 2 in. apart in 5 randomly selected 10-in. lengths of 50% nylon yarns: *a* (top), high twist; *b* (center), medium twist; *c* (bottom), low twist. Solid line, total; short dash line, wool; long dash line, nylon.

method, first by randomizing all 25 sections and taking the range in groups of 5, and then by finding the range within each group of 5 sections of a given 10-in. length. The fact that this latter value is sometimes larger than the former suggests that the extremes of variability may be encountered *within* 10-in. lengths both as to total denier and weight per cent composition for many of the yarns. This point is also graphically illustrated in Figure *7a-c*. This effect, namely, the occurrence of extreme variations within distances of about one fiber length, can be demonstrated graphically by plotting the average difference between numbers of fibers per section vs. the distance between sections.

Offhand one might expect that sections separated by only a fiber length would exhibit close correlation both as to total fiber number and as to blend content. On the other hand, in view of the evidence in the literature for the existence of "drafting waves" which result in short-period high-amplitude fluctuation in yarn weight, one could expect that successive sections at a distance in the order of a fiber length would exhibit negative correlation of fiber content.

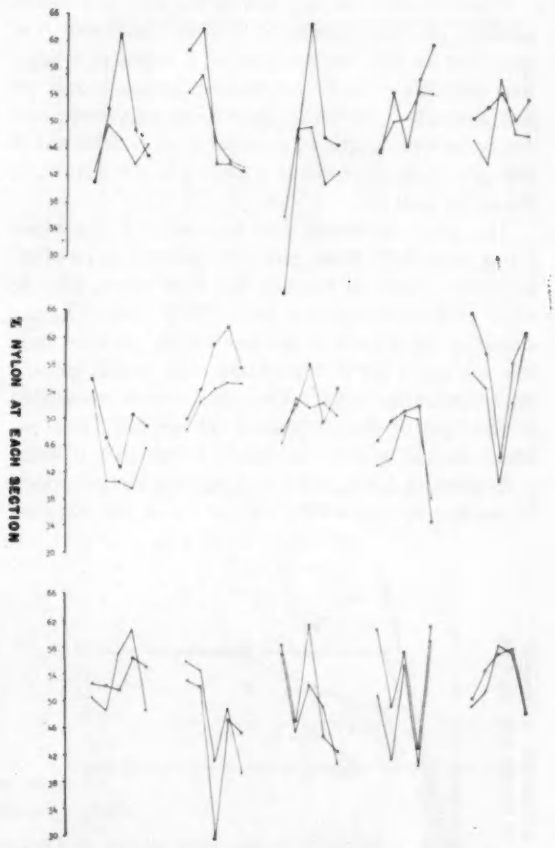

Fig. 7. Nylon concentration of entire section and of interior 50% of entire section at each of 25 sections in 50% nylon yarns: *a* (top), high twist; *b* (center), medium twist; *c* (bottom), low twist. Closed points, total; open circles, inner portion.

It is also conceivable that distances of one fiber length are already sufficiently remote to eliminate the correspondence due to replication, and that the negative serial correlation would not be evidenced for blend distribution.

One can examine this problem by means of a crude form of serial correlogram. The difference in total number of fibers and of each component is found for adjacent sections (i.e., one fiber length apart), sections two fiber lengths removed, three, etc. Then the data for a relatively large number of sections is randomized, and the differences between random pairs are found. If these several differences are averaged for each separation distance, taking all values as positive, they can be plotted as in Figure 8, where only the curves for total fibers are shown.

Curve 1 would correspond to the first alternative, namely, positive correlation between adjacent (i.e., one fiber length) sections; curve 2 indicates a negative correlation between adjacent sections; and the last alternative, in which the maximum average disparity between pairs of yarn sections is achieved at one fiber length, without a negative correlation, is shown by curve 3.

The same treatment can be made of the blend ratio, or of both of the fiber components as numbers of fibers. Such an analysis has been made, and the third alternative appears most nearly correct as exemplified by Figure 9 for one of the yarns. In a few instances there is evidence that trends toward the second alternative. This would seem reasonable in the light of the statistical evidence for clustering which will be given. It should follow that if there is tangling of fibers, once in a while a section which is inordinately enriched will be so at the expense

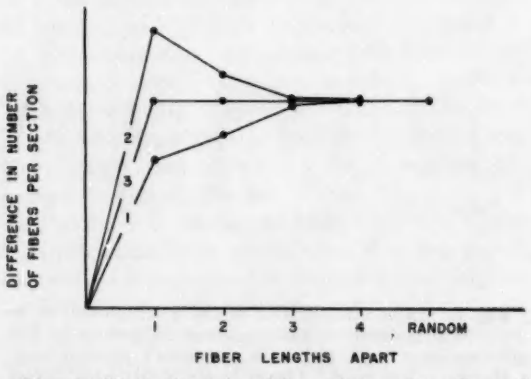

Fig. 8. Illustration of serial-correlation plot. Curve 1 represents positive adjacency correlation; curve 2 represents negative serial correlation; curve 3 shows no adjacency correlation.

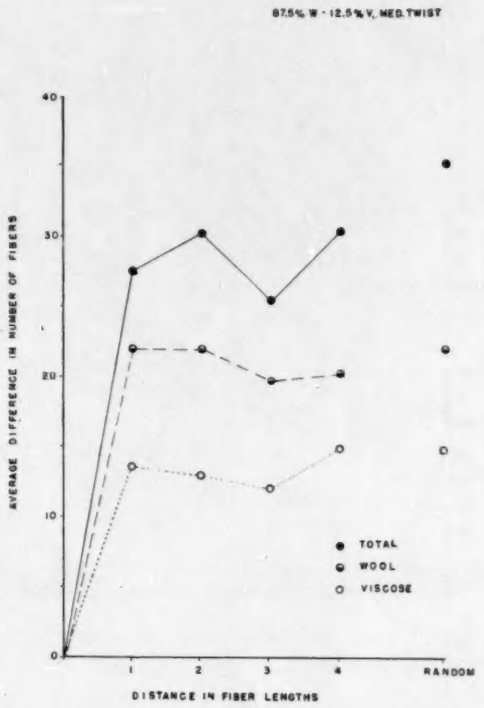

Fig. 9. Typical serial-correlation diagram illustrating indifferent correlation between cross-sections one fiber length apart.

of its successor which, in turn, becomes starved for one of the blend components. This influence should not persist over more than a fiber length, however, and the evidence indicates that it does not, even for the few cases where it was observed at all.

An important question regarding linear distribution of weight and blend remains to be answered. Is there a tendency for the heavy sections in the yarn to contain a generally higher proportion of one or the other of the fibers of the blend? If so, is this effect in any way associated with the fiber content, namely, nylon or viscose, the concentration, or the twist?

Because of the practical and theoretical importance of this matter, data for all yarns tested are presented here graphically. Figure 10 demonstrates rather conclusively that there is no general correspondence between the occurrence of a heavy or thick cross-section and a surfeit of one or the other of wool or nylon in their blends and of wool or viscose in their blends. Neither is any such condition developed as a consequence of added twist. For all the yarns there appears to be only a variation of blend oper-

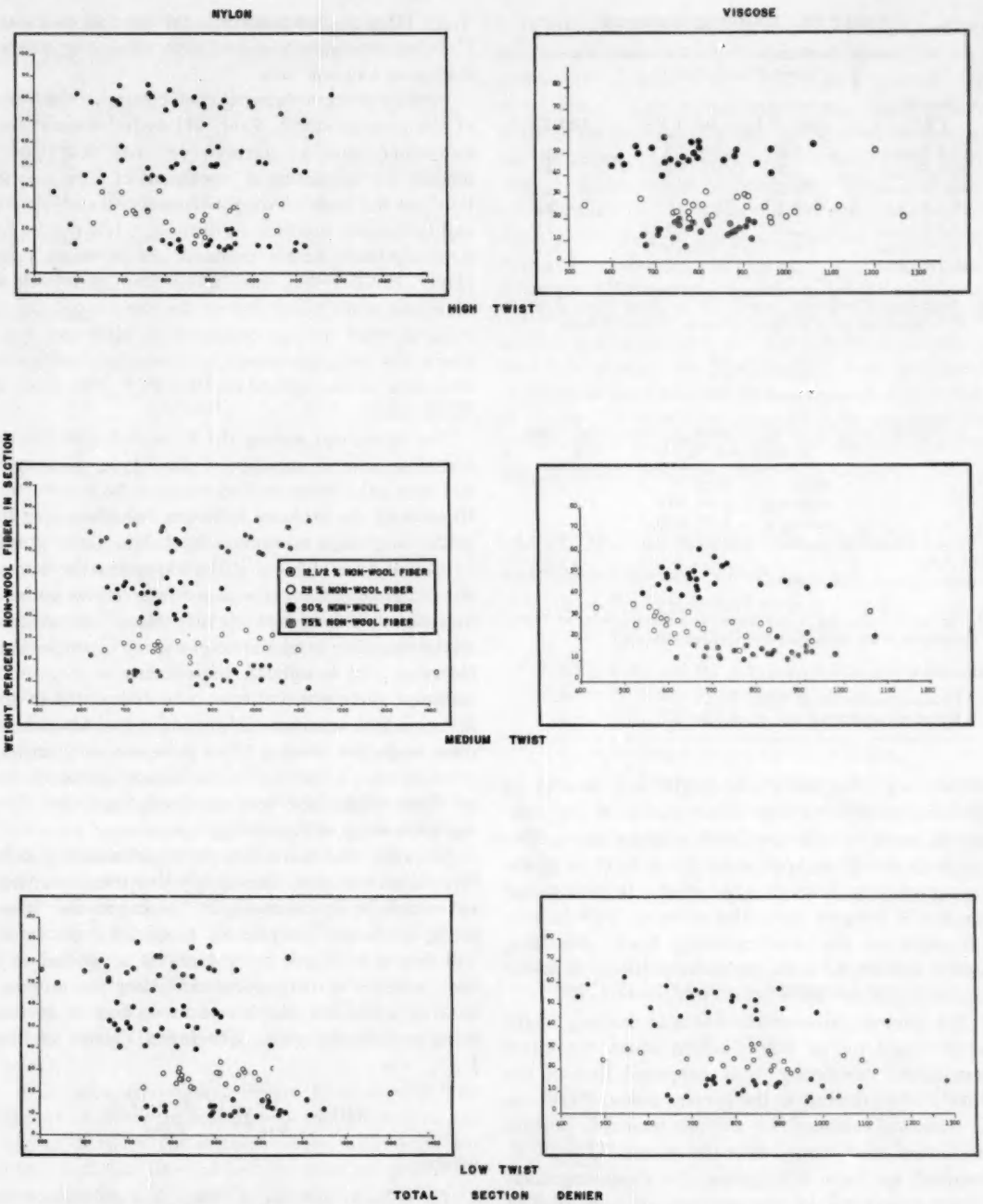

Fig. 10. Plots illustrating that blend concentration and cross-section denier are uncorrelated variables.

ating independently of the variation of total weight. Any inclination of the general pattern of the plotted points in Figure 10 would have suggested otherwise, but the scatter of points is quite horizontal.

This does not intend to convey the idea that *extremely* thick regions, i.e., slubs, would not be preferentially of one kind of fiber. Nor does this information preclude the possibility that other spinning con-

TABLE III. Clustering Coefficients

A. Average Coefficients, C, for Yarns as a Whole, Present Woolen Blends*

Blend (%)	4.5 T.P.I.	9.5 T.P.I.	12.5 T.P.I.
12.5 Nylon	1.6	2.7	1.5
25 Nylon	2.7	3.8	4.8
50 Nylon	3.2	3.2	2.2
75 Nylon	3.4	2.7	3.5
12.5 Viscose	2.3	2.5	2.0
25 Viscose	1.9	2.0, 3.2	2.1, 2.6
50 Viscose	3.6	3.2, 2.4	1.7

B. Individual Coefficients, c and k,† for Each Kind of Fiber, Averaged for All Yarns, Present Woolen Blends

Wool	3.8
Nylon	3.3
Viscose	2.8

C. "Coefficient of Fiber Association, ϕ," for Cotton Yarns, from Grishin [3]

Sliver	63.5
Slubbing	1.05, 10.0
Roving	3.57, 4.30

Yarn: Three-line drafting conditions—2.03, 2.90, 2.94, 2.51, 3.07,1.97.
Double apron—2.17, 2.50.

D. Average Coefficients, C, for Yarns as a Whole, Worsted Yarns, Calculated from Hampson and Onions data [4].

Successive Stages of Roving: 7.5, 7.0, 0.4, 3.3, 2.6, 2.2

* From equation 36 of Part I [5].
† From equations 44 and 45 of Part I.

ditions, e.g., higher draft, might not develop a condition in which a high concentration of one component tends to be related with a heavy spot. This is conceivable if one component tends to resist drafting significantly more than the other. In such a case one would imagine particular sections, high in concentration of the draft-resisting fiber, remaining partly undrafted, while adjacent sections of lower concentration are more completely attenuated.

The tendency toward resistance to drafting might be provoked by, or indeed might cause, the effect here called "clustering." It happened that of the three fibers involved in the present study, there was no statistical evidence that any one tended to operate in clusters much larger than the others. This is illustrated in Table III, giving the clustering coefficients calculated by the methods of equations 44 and 45 of Part I [5]. Since all three fibers exhibit about equal tendency to cluster, preferential drafting would not be expected, and the lack of coincidence of thick spots with superconcentrations of a particular fiber is understandable. At the same time, Table III*A* demonstrates that the over-all coefficient C_1 is not consistently shifted with increasing concentration of any one fiber.

Besides giving clustering coefficients for the yarns of the present study, Table III includes data from two other sources. Grishin [3] has developed a method for calculating a "coefficient of fiber association" on the basis of weight irregularities of ingoing and outcoming products of drafting. His results for some nonblend cotton products are given in Table III*C*. Besides this, data taken from the work of Hampson and Onions [4] on the blend regularity of some worsted rovings composed of white and black fibers has been converted to clustering coefficients according to the method of Part I [5] and given in Table III*D*.

The agreement among the three different sources involving several varieties of fiber type, yarn type, and even calculation method seems to be noteworthy. In all cases the evidence indicates that fibers spin together in groups averaging about 2 to 4 per group.

It should be noted that the clustering coefficients were calculated for yarns as a whole on the assumption that clustering was the only factor operating to inhibit complete randomness of mixing of single-fiber elements. It is difficult to conceive of any other causative situations that cannot be interpreted as due to incomplete separation of the individual fibers from their respective stocks. This does not categorically preclude that a thoroughly randomized blend of single fibers might have been selectively regrouped during some stage of the carding operation.

Allowing that there may be other causes of nonideal blend variation than simply that the fibers were never completely intermingled, the expression "clustering coefficient" may be too broad for general use. The Index of Blend Irregularity is suggested as a basic numerical criterion for evaluating the randomness of blend distribution from section to section along any blended yarn. The Index, derived in Part I [5], was

$$\mathrm{IBI} = \sqrt{\frac{1}{n} \sum \frac{(T_i p - W_i)^2}{T_i p q}} \qquad (1)$$

where

T_i = Total number of fibers at a given section
W_i = Number of wool fibers at that section.
p = Average number fraction of wool fiber for all sections.
$q = 1 - p$.
n = Number of sections examined.

TABLE IV. Index of Blend Irregularity

A. *Longitudinal*

Blend (%)	Twist		
	Low	Med.	High
12.5 Nylon	1.3	1.6	1.2
25 Nylon	1.6	1.9	2.2
50 Nylon	1.8	1.8	1.5
75 Nylon	1.8	1.6	1.9
12.5 Viscose	1.5	1.6	1.4
25 Viscose	1.4	1.4, 1.8	1.5, 1.6
50 Viscose	1.9	1.8, 1.6	1.3

B. *Rotational*

Blend (%)	Twist		
	Low	Med.	High
50 Nylon	1.3	1.3	1.3
50 Viscose	—	1.2	—

For reasonable accuracy, upwards of 10 sections should be examined, depending on the kind of yarn. In the present problem all indices were calculated from 25 sections. These are given in Table IV. It will be remembered that the Index of Blend Irregularity was described as providing a direct approximation of the extent to which a blended yarn exceeded the ideal randomness, with 1 indicating complete randomness, 0 perfect uniformity, and the excess beyond 1 representing the degree of departure from the theoretical ideal.

In the development of the index, certain tacit assumptions were made regarding the general nature of the relationship between the number of non-wools and the total number of fibers. One of these has already been validated: there was no correlation between local values of T and local values of blend composition. One way of saying this is that the value p is a true probability independent of T and that there is a general prediction relationship $W = pT$ (or $N = qT$, where N is the number of nylon fibers).

This point is verified in Figure 11, where the total number of fibers at a section is plotted against the number of nylon (or viscose) fibers. The solid line is the prediction line (or perhaps more accurately the regression line for N on T). Drawn on these graphs in dotted lines are the predicted $2S$ limits. More than 5% of all the points plotted fall outside these limits, as has now been shown numerically by

$$\sqrt{\frac{1}{n}\sum\frac{(T_ip - W_i)^2}{T_ipq}}$$ being greater than 1.

What is of importance is that the graphs confirm the second tacit assumption, namely, that the real points are symmetrically distributed around the trend line. A more rigorous proof would involve analysis for skewness by taking the third moment of the deviation $(T_ip - W_i)$, and for some other practical cases this might be desirable. Thus, it is conceivable that the longitudinal distribution of blend in some yarn could be fairly uniform for most points with only occasional high-concentration regions appearing. This does not appear to be the case here.

In any event, the C. V. of per cent composition is another statistical criterion that can be employed to ascertain whether the experimental yarns conformed to the ideal random blend in longitudinal distribution of fibers. It would be interesting to compare the C. V.'s given in Table II with the theoretical C. V. for the blends calculated according to

$$\text{C. V.}_{\%\text{ nylon}} = 100\sqrt{\frac{\omega}{\alpha}\frac{1}{\bar{D}}(\alpha\bar{d}_w + \omega\bar{d}_a)(1 + x)} \qquad (2)$$

which was discussed in Part I.

ω = Wt. fraction of wool in blend.

α = Wt. fraction of other fibers in blend.

$\alpha + \omega = 1$.

$\bar{D}$ = Average yarn denier.

$\bar{d}_w$ = Average denier of wool fibers.

$\bar{d}_a$ = Average denier of other fibers.

$(1 + x)$ = A function of total weight irregularity having values rarely in excess of 1.05.

This comparison is made in Table V, where the actual C. V.'s are taken from table II and averaged over the three twists. Similarly, the I. B. I. values

TABLE V. Statistical Evaluation of Longitudinal Blend Irregularity for All Blends, Averaging Three Twists

Blend Composition	C. V. of Wt. % Nonwool Fiber (%)		Ratio of C. V.'s Actual/ Ideal	Index of Blend Irreg.
	Actual	Ideal*		
12.5% Nylon	25.6	16.5	1.6	1.4
25% Nylon	19.1	11.0	1.7	1.9
50% Nylon	12.0	6.5	1.8	1.7
75% Nylon	6.7	3.9	1.7	1.8
12.5% Viscose	23.5	16.0	1.5	1.5
25% Viscose	19.6	10.6	1.8	1.5
50% Viscose	11.3	6.5	1.7	1.6

* Using $\bar{D} = 900$. $\bar{d}_n = 3.4$. $(1 + x) = 1.02$. $\bar{d}_v = 3.1$. $\bar{d}_a = 4.3$.

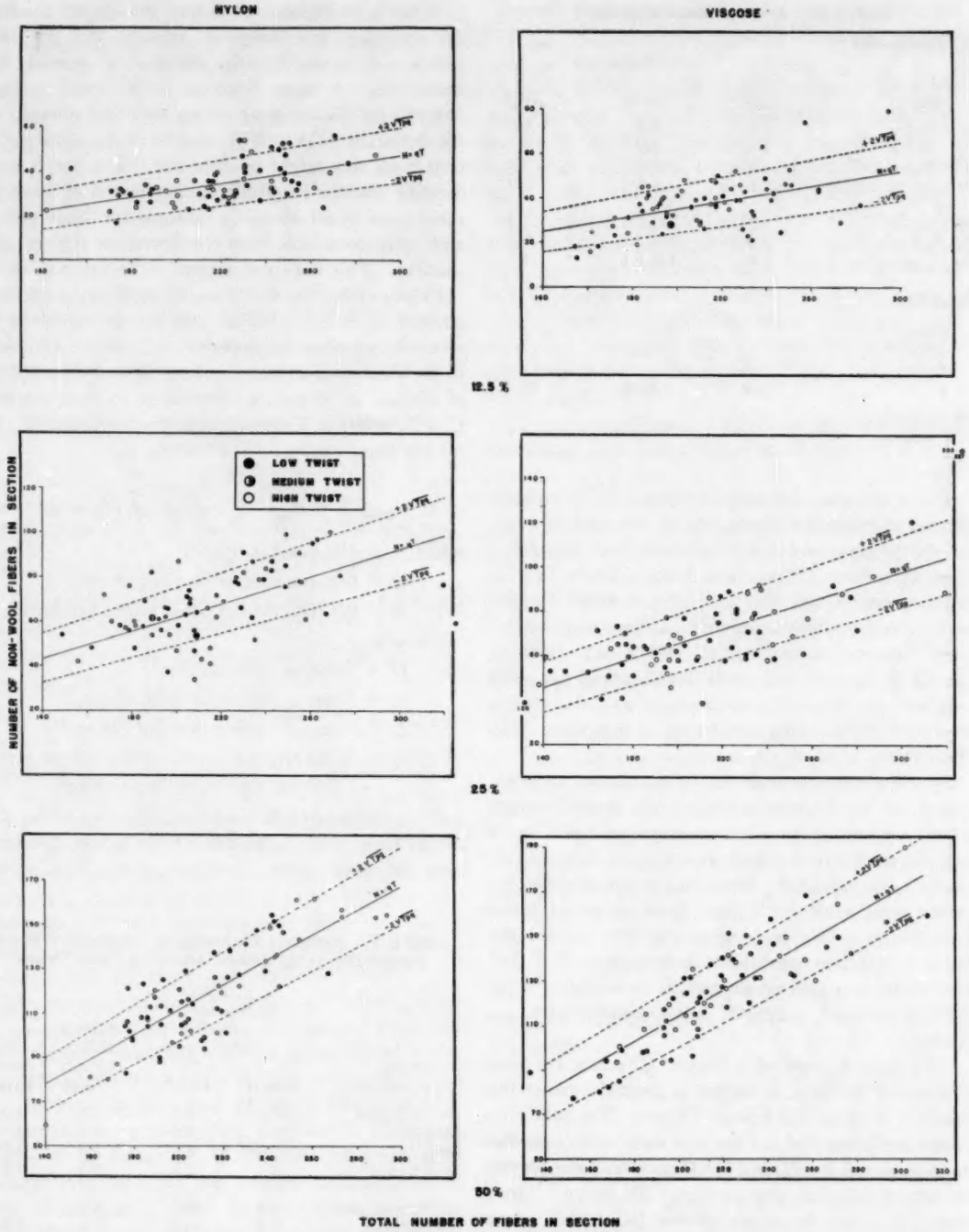

Fig. 11. Plots illustrating the dependence of number of nonwool fibers at a section on the total number at the section and the symmetrical dispersion around the proportionality line.

shown are the average for three twists from Table IV. Averaging the three twists appears justified in view of the indifferent effect of twist revealed so far by the data of Tables II and IV. It will be seen that either criterion yields essentially the same information, namely, that the blends are 1½ to 2 times as irregular as would be expected from completely random mixing.

It is apparent that by both calculations illustrated in Table V the system which produced the yarns either failed to mix the fibers as single elements in a random fashion or, that having been done, some subsequent steps tended to cause a longitudinal "separation" of the components. The former possibility is by far the most likely, both from the point of view of the spinning process and by analysis of other statistical data on "clustering" of fibers based on examination of blend distribution *within* cross-sections.

The foregoing analysis of longitudinal-blend distribution considers the composition at each cross-section in its entirety. Within-section blend distribution is equally important and is to be considered next.

B. Radial Characteristics

Examination of within-section blend distribution can be made in terms of rational areas or by reference to lines of symmetry drawn on the projected image of each yarn cross-section. This procedure permits graphical treatment of the data to a greater extent than is possible for the longitudinal-blend information.

Consider now only a single yarn cross-section. Allow that the "center of gravity" can be found and draw concentric circles on the section in such a fashion that each successive ring encloses one unit area (or some simple multiple of unit area). The number of each kind of fiber in each radial area can be determined, starting at the center and working toward the periphery. Since areas in all sections will be taken with reference to the same point of symmetry, namely, the "center of gravity," it will be possible to find for the entire yarn the average "core" concentration. Figure 7*a-c* gave some indication of a tendency for wool to prefer the outer 50% of the yarn, for example. Generally speaking, the average blend-distribution pattern from inside to outside of the yarn for any number of whole cross-sections studied can be ascertained.

If there is a preferred position for one of the two kinds of fibers in a blend, the average radial distribution pattern should show this up. The data will be quantitative as well as graphical, although the average effect observed will be limited in reliability by the variability from section to section and the total number of sections examined. The method employed in developing Figure 12 warrants some explanation.

Consider any one cross-section. Find the blend weight per cent composition. Now, determine the blend composition of the innermost area of the section. Find the difference in composition of this inner area from that of the whole section. Proceed to the next concentric area and combine it with the center of the yarn. Compare the blend composition of the new combined areas with that of the whole section. Continue outward, integrating the newly added regions with the interior, and compare the blend compositions at each successive radius until the entire yarn is encompassed. Obviously, at the time the outermost regions have been integrated with the then interior part of the yarn, the blend composition will be identical with that of the whole section.

Now, reverse the procedure, considering only the outermost anulus first. Find the difference between its composition and that of the whole section. Progress inward, integrating the next ring, and repeat the procedure until the entire section has again been traversed, but this time from outside inward.

Now, plot the deviation from the whole blend composition as found for each successively integrated region inside-outward from left toward right 0 to 100% of the entire yarn weight. Then plot the integrated effect from outside inward from right to left 0 to 100% of yarn weight. The two curves fuse at 100% and 0 deviation (see Figure 3). The deviations thus plotted in absolute units of per cent composition for a series of sections can be directly averaged together, taking due account of the direction of the deviations found for each area of all sections.

Consider on Figure 12 the vertical half-circle points identified in the legend with the 75% wool–25% nylon low-twist yarn. The farthest point to the left falls at the inside 20% of total mass and + 5% deviation. This point (and all others) is the average of all 25 sections of the particular yarn in question. It indicates that the innermost 20% of the yarn averages 5% (absolute units) blend composition higher than the average of the entire blend. In other words, the inner 20% of the total yarn weight is 70% wool and 30% nylon, although it is overall

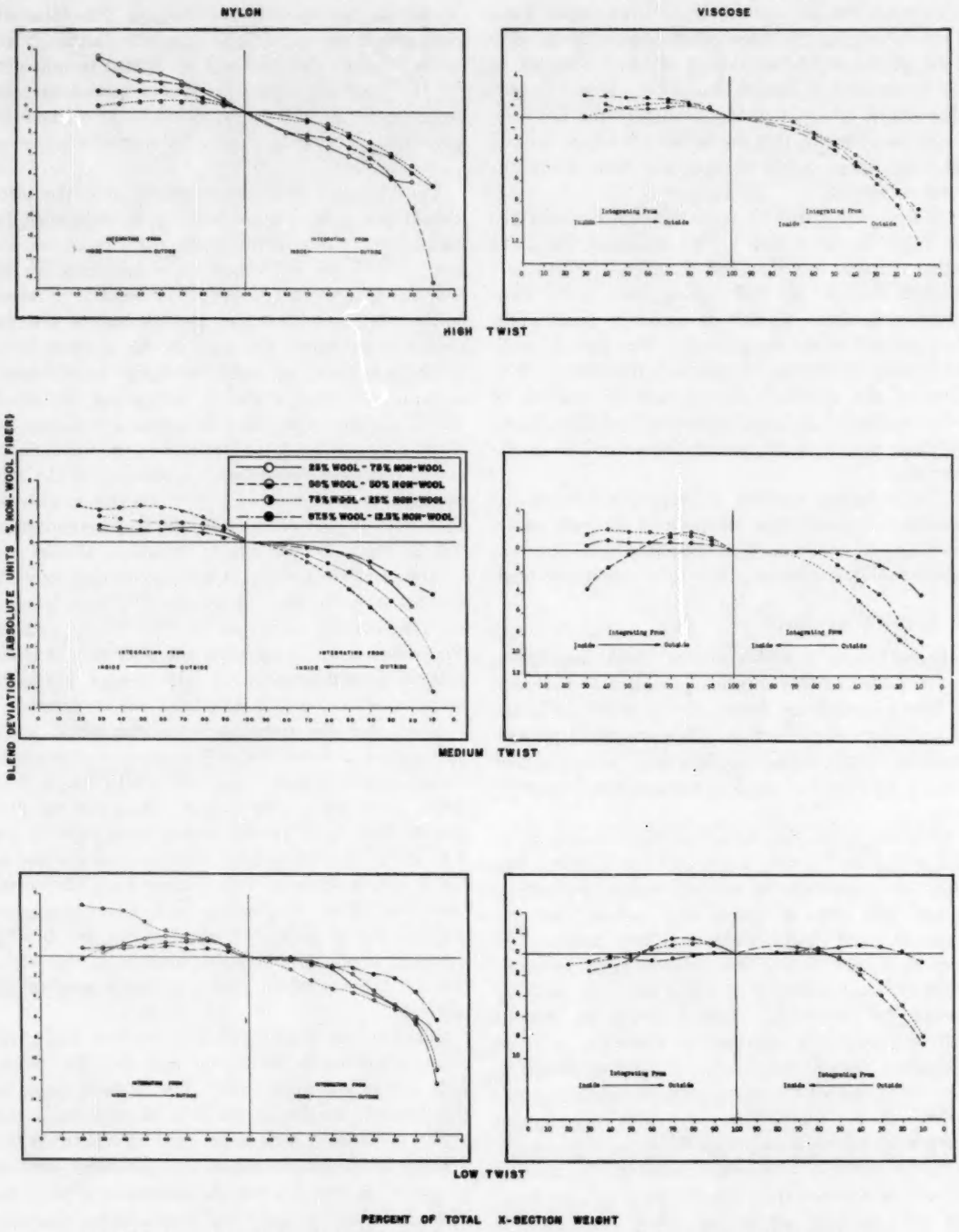

Fig. 12. Plots of blend deviation of concentric areas illustrating the tendency toward fringe deficiency of the nonwool component.

a 75%–25% yarn. The inner 70% of the entire yarn averages 2% higher (i.e., 73% wool and 27% nylon). The inner 90% averages about 74% wool and 26% nylon.

These last figures may seem insignificantly different from the overall 75%–25%, and if the curves were to be ended after integrating only from inside to outside a misleading picture might result. Therefore, the same data is reintegrated from the outside inward. It does not actually present *new* data, but it seems to provide a more dramatic picture of the state of affairs.

Consider the farthest point to the right of the same yarn, now. It falls at the outside 10% of total mass and at − 11% deviation. This signifies that on the average the outermost 10% by weight of the 75%–25% wool-nylon yarn is only 14% by weight nylon. The outermost 30% by weight of the entire yarn is only 20% nylon, etc.

These curves lead to conclusions of major practical significance. They indicate, for example, that the surface (say outer 10–20%) of all of the wool-nylon yarns in this series runs consistently lower in nylon concentration. Any behavior characteristic of such yarns which depends on the surface properties must be interpreted in this light. Abrasion resistance is one such property. Bending and torsional stiffness are two others.

In the nylon-wool series there seems to be no association of twist with either the general "inside-outside" pattern or the magnitude of deviation involved. Composition, however, seems to have a minor influence on the magnitude of the effect. It will be seen that the 50–50 wool-nylon yarns in all three twists exhibit the highest absolute deficiency of nylon in the outermost fringes of the yarn. Also, the 87.5% wool yarns consistently exhibit the lowest deficiency in absolute units of per cent nylon. On the other hand, the *relative* effect is reversed and may be considerably more significant, since obviously a 7% nylon exterior shell on a nominal 12.5% nylon yarn is proportionately a more marked departure than a 38% nylon exterior shell on a 50% nominal yarn.

The low- and medium-twist viscose blends exhibit a more erratic effect than the nylon blends. Although there remains a definite indication of excess wool in the yarn exteriors, the effect dwindles rapidly on moving inward, and the blend attains that of the average after no more than half of the outer regions have been encompassed. In fact, the inner half of several of these yarns shows a very slight excess of wool in contrast with all of the wool-nylon yarns, where none show other than excess nylon.

There apparently also is an influence of twist on the whole pattern in the wool-viscose blends. The high-twist yarns exhibit a definite continuous gradient in the radial-blend distribution. It appears that, irrespective of the behavior of their lower-twisted counterparts, the high-twist viscose blends behave much like the wool-nylon blends at all twists.

The determination of exact causes of such phenomena as just described is not the prime purpose of this analysis. Nevertheless, an explanation seems to be in order here. It is suggested that the apparent deficiency of nylon and viscose in the outer shells of all these yarns is in reality an excess of wool; that is, the pattern is more nearly one of "fringe deficiency" rather than "core concentration" (see Figure 3).

It is believed that the generally higher than expected concentration of wool in the yarn exterior is due to the peculiar morphology of the wool fibers. These have, as is well known, a decidedly multidirectional crimp. A single wool fiber would occupy a "cylinder of space" considerably greater than its own solid volume. For the most part the man-made fibers are produced with essentially monoplanar crimp. The volume in space which a single nylon fiber might tend to occupy would more nearly approach the actual solid volume of nylon.

Consider, then, what occurs when a group of nylon and wool fibers are thrown together with their long axes parallel. The probability of finding a portion of a wool fiber on the outside of the bundle at any point along the length of it would be greater than the number proportion of wool fibers in the bundle.

Twisting such a bundle might redistribute the wool and nylon is some fashion depending on the relative rigidities of the fibers, with less stiff ones being forced to accept more "uncomfortable" positions than the stiffer ones. This pressupposes that the fiber elements have the freedom to move preferentially around or past one another during twisting. The possibility of this occurring is not to be completely discounted by any means, but it is here suggested that in the original untwisted state wool has already assumed a position toward the outside of the fiber assemblies.

There are several questions to be answered in regard to radial distribution patterns. For example, is there any trend which would indicate that the departure of the concentration of nylon or viscose in

the center from the average of the yarn is associated with either heaviness or lightness of the particular section? Figure 13 illustrates that there is no such trend. The deviation of the interior concentration from that of the whole section is not influenced in any consistent or trendwise pattern by the total instantaneous cross-section denier. This is true for both the nylon and the viscose blend series.

C. Rotational Characteristics

Whereas the radial areas could be directly averaged together by orienting them with reference to a common axis of symmetry, this is not feasible for rotationally arranged areas. The "center of the yarn" has a descriptive meaning at any cross-section. But the "top of the yarn" is an entirely arbitrary location for each section.

This would not be an impossible condition to rationalize if it were necessary or even desirable. It is of little value, however, to talk about the average blend composition of the "top half" of the yarn, or some such figment, since the yarn in process and in simple handling does not behave as a ribbon, always presenting its top surface to examination. Moreover, the "top" at any one point in a spun staple yarn is entirely disassociated from the "top" or any other rotationally located region at some other section beyond a fiber length or even less. Just the normal variation of twist will prevent a rational grouping of rotational areas from section to section on the basis of angular displacement from some arbitrary "top" point.

In spite of this, nevertheless, examination of rotational-blend distribution is desirable and certainly possible if one considers each whole section at a time. It is also possible to examine certain effects by recourse to statistical methods similar to those applied to longitudinal properties.

Each yarn cross-section is divided into octants, numbered sectors 1 through 8, purely for convenience. It is understood that sector 1 in one cross-section has nothing topological in common with sector 1 of some other cross-section. The blend composition for each entire section has already been determined, and now the blend composition of each octant can be found. The data are treated three ways.

First, a statistical examination of rotational-blend composition is made by finding, for each octant:

$$t = \frac{(R_i p' - w_i)}{\sqrt{R_i p' q'}} \qquad (3)$$

where

p' = Proportion of wool in whole section.

$q' = 1 - p'$

R_1, R_2, etc. = Total number of fibers in sectors 1, 2, etc.

w_1, w_2 = Number of wool fiber in sectors 1, 2, etc.

Values of t thus found for each of the sectors of all sections are all plotted together in a frequency curve. The mean of this curve should fall on 0; the standard deviation should be equal to 1; and the shape should approximate the normal Gaussian distribution if there is only a random rotational distribution of blend. Marked departures from this will be indicative of certain forms of blend disturbance. For example, decided bimodality of this curve indicates sharp separation of the two blend components in a rotational pattern. Skewness suggests a tendency of one of the components to aggregate, leaving the other regions of the yarn partly deprived of this kind of fiber. "t" distributions for three of the yarns are shown in Figure 14. If there had been a pattern of superconcentration of nylon in particular sectors of the sections, these frequency diagrams would be sharply skewed. If there had been a pattern of very patchy alternation of wool and nylon, these diagrams would exhibit bimodality.

Neither condition is observed. The diagrams all seem reasonably symmetrical with the modal value on the mean, 0. In other words, the evidence is in favor of the proposition that there is a sector high in wool as often as there is one high in nylon and that the extent of departure from the average blend composition is about the same for either condition.

A minor effect of twist on this pattern seems fairly clear. Evidently, increasing twist results in somewhat closer approximation to rotational-distribution symmetry. This symmetry is directly reflected in the increased peakedness in the lower diagrams of Figure 14.

There is also a quantitative significance that can be attached to values of "t." Actually, the root mean square of all "t" values is equivalent to the Index of Blend Irregularity, except that here it is taken for rotational subsections rather than for whole sections.

The validity of this calculation is limited by the prescription that $R_i p' > 5$, for $p' \leqq 0.5$. This condition is met most completely only in the 50–50 blends, where R generally exceeds 20, and p' exceeds 0.3. It is not a useful technique, therefore, in most cases involving minor blends. The average of all values of t^2 may also be found and here, as in equation 36 of Part I, a coefficient of clustering is found.

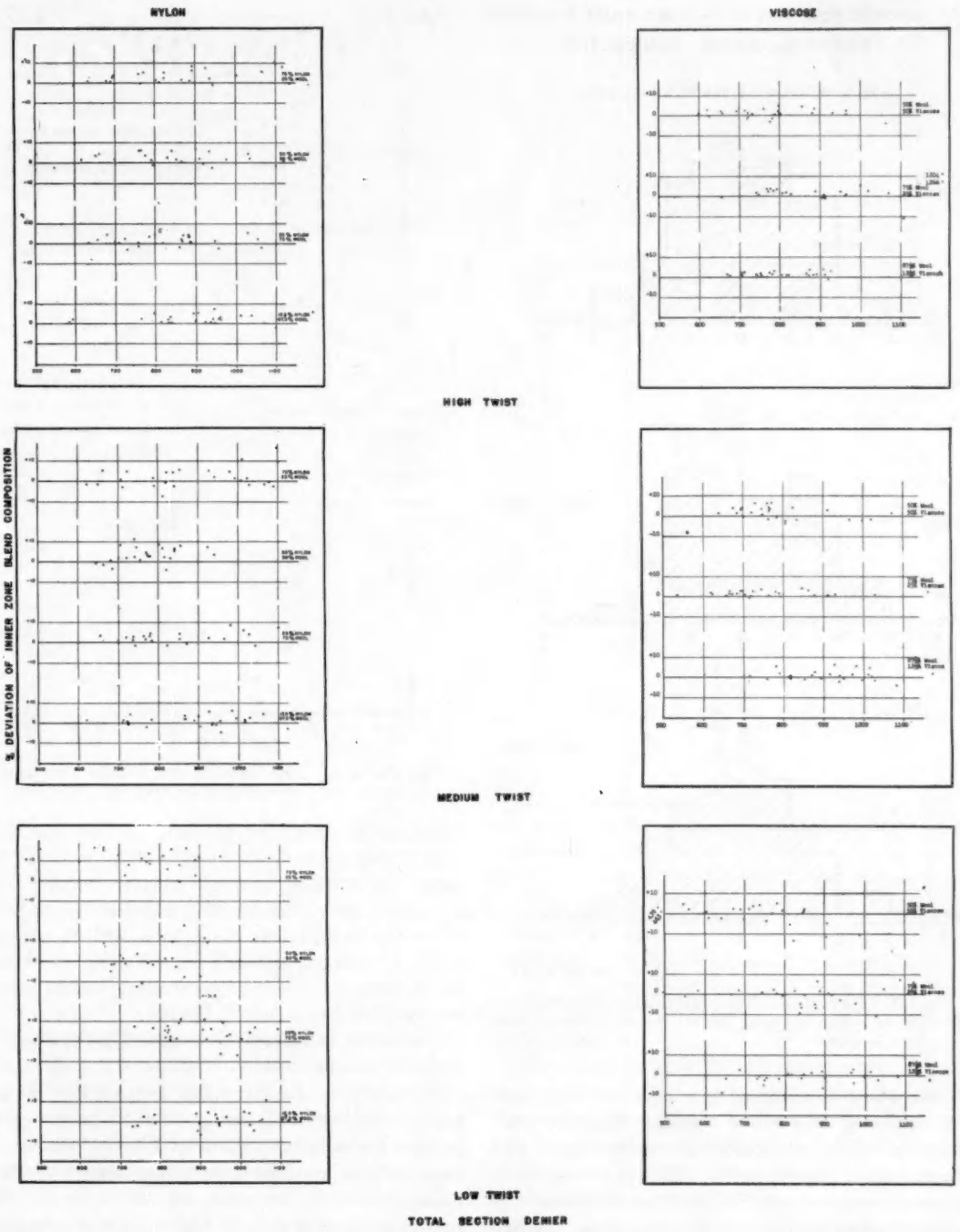

Fig. 13. Plots of blend deviation of inner zone of yarn vs. total section denier illustrating that inner-half concentration is uncorrelated with total section denier.

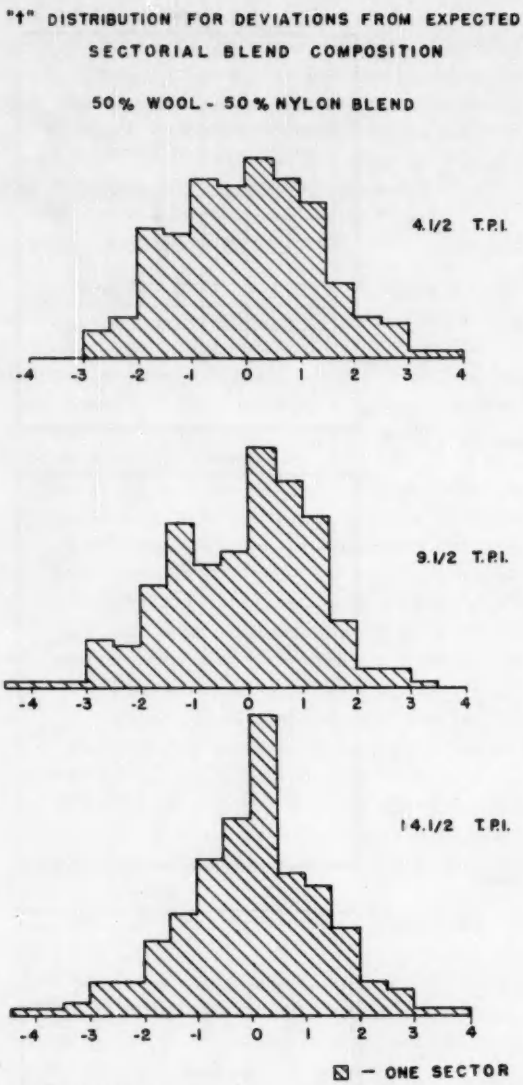
"t" DISTRIBUTION FOR DEVIATIONS FROM EXPECTED SECTORIAL BLEND COMPOSITION
50% WOOL - 50% NYLON BLEND
4.1/2 T.P.I.
9.1/2 T.P.I.
14.1/2 T.P.I.
-4 -3 -2 -1 0 1 2 3 4
▨ — ONE SECTOR

Fig. 14. Illustration of the symmetrical rotational distribution of nylon; as many sectors low in nylon as there were high in nylon.

One would not necessarily expect that the apparent clustering or running together of fibers longitudinally in the yarn would be identical with that found within cross-sections. While a pair of fibers is constrained, because of entanglement, to move together through the card, on the rub aprons, and into a particular portion of the yarn, this does not necessitate that the pair will always be found as adjacent

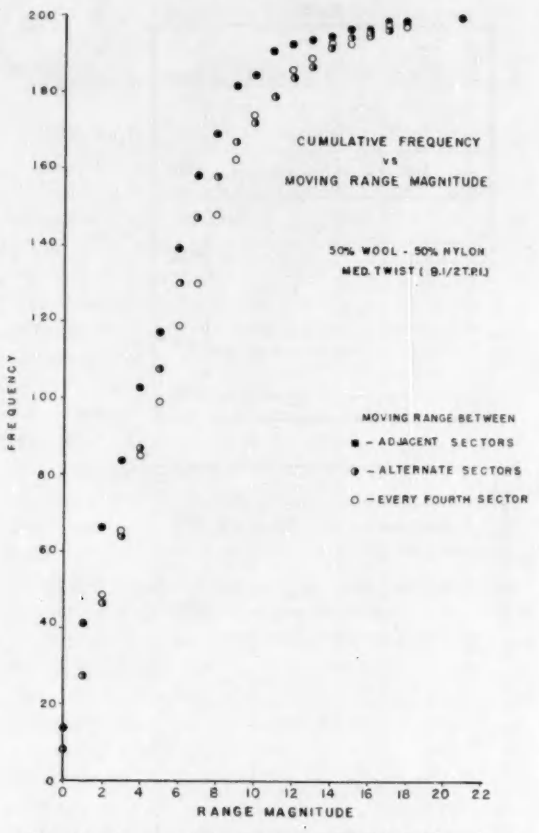
CUMULATIVE FREQUENCY
vs
MOVING RANGE MAGNITUDE
50% WOOL - 50% NYLON
MED. TWIST (9.1/2T.P.I.)
MOVING RANGE BETWEEN
■ — ADJACENT SECTORS
◑ — ALTERNATE SECTORS
○ — EVERY FOURTH SECTOR
FREQUENCY
RANGE MAGNITUDE
0 20 40 60 80 100 120 140 160 180 200
0 2 4 6 8 10 12 14 16 18 20 22

Fig. 15a, b, c. Plots showing that within X sections adjacent sectors were more alike than remote sectors.

neighbors at every section where the two both appear. Frequently, such fibers will be expected to appear in different sectors. This is probably the case, since the clustering effect found by the method of sectorial subdivision of the yarn sections ran between 1.5 and 2.0, although the clustering coefficient for the same yarns found from the longitudinal analysis ran from 2 to 4 (see Table III).

Two other techniques were applied to the analysis of rotational distribution, both concerning a serial-correlation effect similar to that mentioned for longitudinal distribution. The question to be answered is this: Do adjacent sectors tend to correspond in blend content or does a particular sector, of high nylon content, for example, tend to be flanked by sectors deprived of nylon? One method of analyzing for this possibility employs the "moving range."

The difference in the number of nylon fibers was

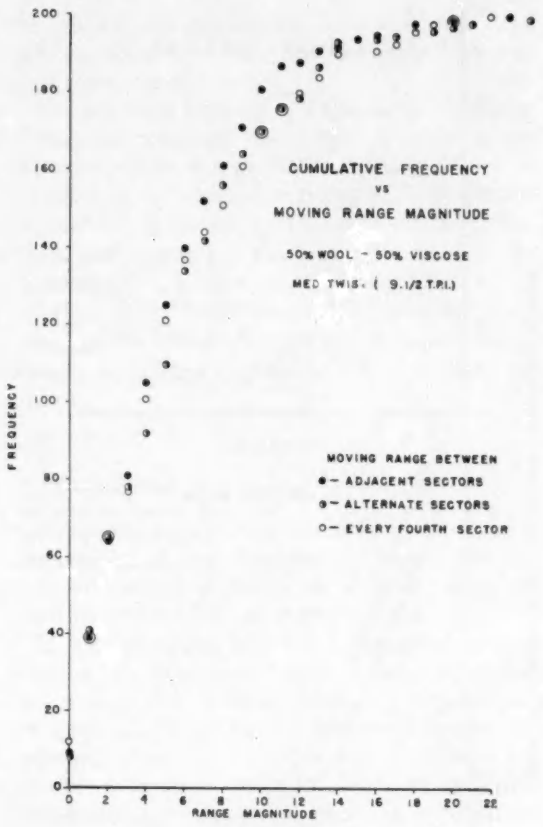

Fig. 15b.

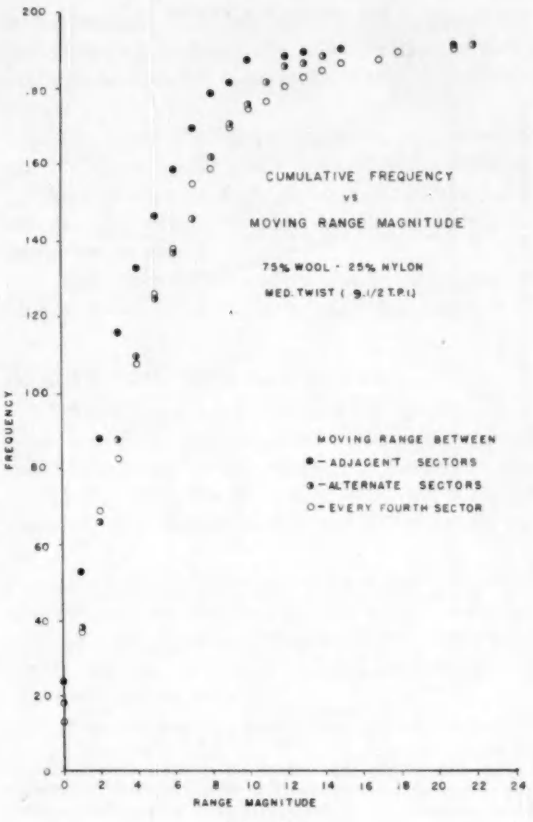

Fig. 15c.

found between all adjacent sectors, between all sectors once removed, and between each pair of sectors diametrically opposite. These differences were plotted as cumulative frequency curves.

The "moving range" curves for three yarns are shown in Figure 15*a-c*. Here the average net difference in numbers of nylon or viscose fibers between paired sectors is plotted as a cumulative frequency curve for all sectors in 25 sections. Consider the three points directly above "Range Magnitude" 2 for the 50% nylon medium twist yarn on Figure 15*a*. They indicate that 65 out of 200 pairs of adjacent sectors differed by only 2 fibers in nylon content, while alternate and opposite sectors differed by 2 fibers in only 45 out of 200 pairs. All three graphs indicate the same effect qualitatively, namely, that adjacent sectors tended to be more alike than did sectors more remote.

The general average effect of adjacency correlation may also be illustrated graphically by another procedure, as follows. Find the particular sector in each section which contains the highest accumulation of nylon fibers. Call this sector 1 and number all other sectors accordingly. Now, 2 and 8 are the adjacent neighbors of 1; 3 and 7 are once removed, etc. But so far as the analysis of adjacency is concerned, 2 and 8 are equivalent to one another, as are 3 and 7, etc.

Now, for all cross-sections taken, average together the number of nylon fibers in all sectors designated 1 by this method; those in the 2 and 8 pairs, etc. Plot the average number of fibers per sector so found vs. the sector number.

Alternatively, count the total number of nylon fibers in the entire section and the number in each sector. Find the difference between $\frac{1}{8}$th of the total number and the actual number found for each sector.

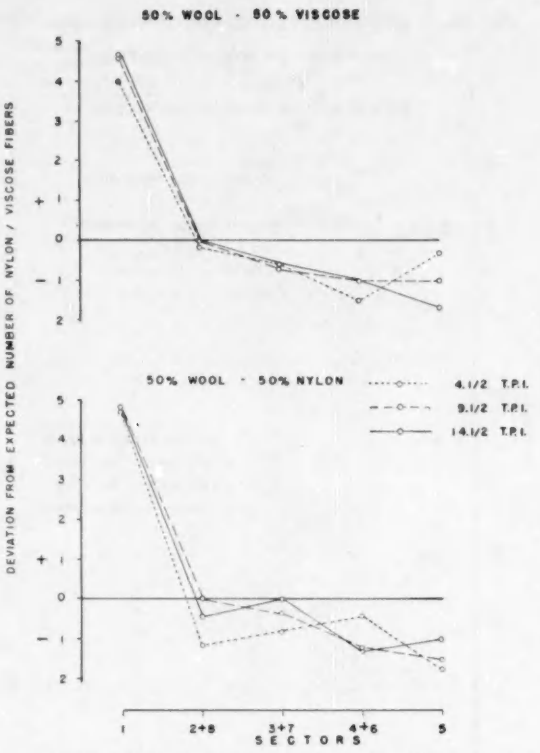

Fig. 16a. Plots illustrating that sectors adjacent to the one of highest nylon composition were in general of average blend composition. *a* and *b* give same general information, using slightly different ordinates.

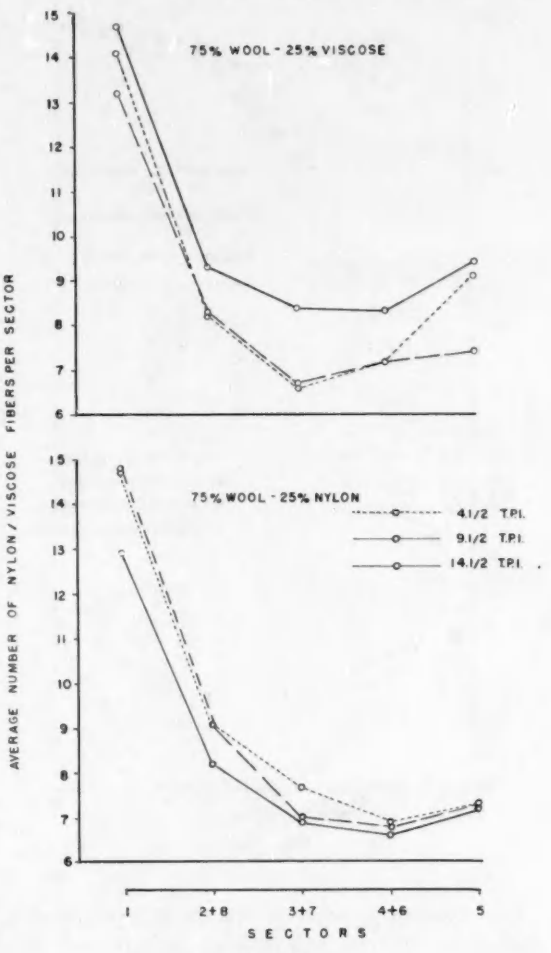

Fig. 16b.

Plot this deviation vs. rotational position, starting from the sector of highest positive deviation.

Figure 16*a* was plotted in units of deviation of number of fibers, and Figure 16*b* employed the actual number of fibers. The two are equivalent, but perhaps the former is a little more informative. Examine Figure 16*a*. It will be seen that on the average the sectors (2 and 8) immediately adjacent to that having the highest concentration tend to contain no more or less than the average number of fibers per section. All other sectors for the 50–50 viscose yarns are weak in viscose concentration. For the nylon there is a similar, although less pronounced, trend.

It can be said of the 50–50 yarns, therefore, that high concentration of viscose or nylon at one rotational position gradually tapers off around to the regions of lower concentration. It should be immediately emphasized that these "adjacency correlation" figures do not signify that there is in every section a region decidedly higher in concentration than all the others. The picture developed here of unisectorial concentration is entirely due to the method of registering together the sectors of highest concentration first. A similar impression of unisectorial deficiency could be had by registering all the lowest concentration sectors together. The diagrams should only be interpreted as so far indicated, namely, that on the average when there is a region higher in concentration than the average its adjacent neighbors are not particularly depleted. On the contrary, they tend also to be somewhat higher in concentration than all other sectors. This is the effect to be noted in Figure 16*a* and *b*. The deficiency of nylon or viscose which must appear as a consequence of

the excess at one spot tends to occur at regions about half way around the yarn from the original point of high concentration.

The combined evidence of Figures 14, 15, and 16 is that the rotational distribution of blend is not characterized by any particular tendency of one or the other of the fibers to aggregate in large clusters on one side of the yarn. However, complete rotational randomness has not been achieved since the rotational I. B. I.'s are approximately 1.3.

In the three 50–50 wool-nylon yarns the fibers seem to be distributed within cross-sections as though in average clusters of 1.5 to 2 fibers per cluster.

Summary

A. Longitudinal Distribution

1. On the average, maximum deviation in blend composition of some woolen-type wool-nylon and wool-viscose yarns occurs at distances along the yarn as short as one fiber length apart.

2. The deviation in blend composition between sections one fiber length apart is only occasionally larger than that found by comparing random pairs of sections. From this it is concluded that, on the average, the excess of one fiber component at a particular section is not directly the cause of a deficiency in the next adjacent section, except in some isolated instances.

3. An Index of Blend Irregularity indicates that for all the yarns examined the degree of mixing is poorer than could be expected for the ideal random yarn. This Index ranges from 1.5 to 2.0, where the value of 1.0 would indicate perfect randomness; 0 represents perfect uniformity; and the excess above 1.0 is a direct quantitative measure of the average overall excess inhomogeneity beyond randomness.

4. The cause of the nonideal randomness of blend is here ascribed to incomplete separation of the original fiber stocks into single-fiber elements. A clustering coefficient is calculated which indicates that on the average the fibers seem to be operating in groups of two to four.

5. The extent of this clustering is not greatly different among the three kinds of fibers involved. Individual coefficients for each fiber type average 3.8 for wool, 3.3 for nylon, and 2.8 for viscose.

6. The blend concentration at a given section is uncorrelated with the total number of fibers found at that section. This does not exclude the possibility that slubs may preferentially be of one type of fiber, although no evidence is presented either way in this respect.

7. The blend distribution appears to be symmetrical; i.e., there are as many sections with excess of one kind of fiber as there are sections exhibiting a deficit. The extents of these conditions appear to be similar in magnitude.

8. There is no notable effect of average yarn twist on any of the blend characteristics just noted.

B. Radial Distribution

1. There is a general tendency for the peripheral regions of all yarns examined to have more wool than the nominal average blend. The extent of this is such that the outer 20% of 12.5% nylon yarn, for example, may contain as little as 7% nylon on the average.

2. The effect of average yarn twist on radial-distribution patterns is nil for the nylon blends and not great for the viscose yarns. In the latter case, the increase of twist to 14½ t.p.i. accentuated the described pattern somewhat.

3. The radial-blend-distribution pattern seems to be uncorrelated with the total weight of fibers at the section in question.

C. Rotational Distribution

1. Adjacent rotational regions within given cross-sections are, on the average, more like each other than are remote regions, but the evidence is against pronounced "one-sidedness" of blend dispersion within cross-sections.

2. The pattern of rotational distribution seems to be nearly random except for the residual effect of clustering noted for the longitudinal direction.

3. The extent of departure from ideal randomness of blend distribution within sections can be gaged from the rotational Index of Blend Irregularity value of about 1.3 found for 50–50 wool-nylon yarns, in twists 4½, 9½, and 14½ t.p.i.

4. In these three yarns the effect of twist on Index of Blend Irregularity was negligible. It is therefore concluded that merely twisting an already established aggregation of fibers does not particularly disturb their relative positions as measured rotationally.

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Penetration of Alkaline Solutions into Wool Fibers Determined by Changes in the Rigidity Modulus

Marianne Kärrholm, Gösta Nordhammar, and Ove Friberg

Abstract

An apparatus is described for determination of the torsional rigidity and rigidity modulus of textile fibers. The apparatus is a modification of the torsion pendulum and is especially suitable for determination of changes in torsional moduli, e.g., after some treatment.

Tests have been made on wool fibers subjected to treatments with either potassium hydroxide in ethanol or sodium hydroxide in butanol kerosene. In the first case the rigidity modulus decreased about 10% on account of the treatment, while no change occurred in the second case. The rigidity modulus is a much more sensitive indicator of changes in the outer parts of the fiber than is Young's modulus.

In connection with an investigation of the influence of fiber friction on the crease recovery of wool fabrics, we found that treatment with alcoholic potash decreased the crease recovery of the fabric, while treatment with sodium hydroxide in butanol kerosene had no effect on this property. The change in the coefficient of friction was the same in both cases, however. It is therefore reasonable to assume that not only the surface properties but also the mechanical properties of the fibers are changed by the treatment with alcoholic potash.

A method originally proposed by Burte [1] was used to investigate whether this is so. The Hookean slope in water was determined for the same fiber before and after the treatment. The effect of variations in cross-sectional area between different fibers is eliminated by this method. However, the same value of the Hookean slope was obtained before and after treatment. Investigations made by Lindberg [4] have also shown that alcoholic potash does not cause any changes in the stress-strain properties of wool fibers.

In stretching experiments all parts of the cross-section are subjected to the same tension. Outer parts of a fiber subjected to torsion are given larger deformations than inner parts. The torsional rigidity of a fiber is thus more sensitive to changes occurring mainly in the outer parts of the fiber than is the stiffness determined from stretching experiments.

We have therefore designed an apparatus especially suitable for determination of changes in torsional rigidity. Measurements can be made on the same fiber before and after a particular treatment. The apparatus can also be used for absolute measurements of the modulus of rigidity.

Design of Apparatus

The modulus of rigidity is defined as the ratio of the shear stress to the shear strain. For thin threads this modulus may conveniently be determined from experiments with a torsion pendulum. The most commonly used type of torsion pendulum consists of a thread and a suspended body connected to the lower end of the thread, while the upper end is fixed. The period of oscillation is observed, and, if the length of the thread and its polar moment of inertia are known, the modulus of rigidity can be calculated. The period of oscillation is also dependent on the moment of inertia of the suspended body, but this quantity is a constant and need only be determined once.

If the thread is very thin, the weight of the suspended body may cause considerable tension in the thread. To avoid this, a modification of the conventional torsion pendulum was employed, consisting of two vertical coaxial threads.

The suspended body hangs on a suitable filament, e.g., a thin metal wire, and the test thread is at its *upper end* attached to the body, while the lower end is fixed. The two threads thus form two parts of a common axis of rotation with the suspended body between them (see Figure 1). The tension in the test thread can be chosen almost arbitrarily, and the apparatus was designed to test the same fiber before and after some treatment.

The suspended body, regardless of its weight, can be given dimensions that will give a suitable period of oscillation and an easy mounting of the fiber.

Theory

The following symbols are used:

T = Period of oscillation, sec
I_b = Moment of inertia of the suspended body, d cm sec^2
I_t = Polar moment of inertia of the thread, cm^4
M = Restoring torque, d cm
α = Angle of twist, radians
D = Moment of torsion = M/α
G = Rigidity modulus, d/cm^2
r = Radius of the thread, cm
L = Length of the thread, cm

For the simple torsion pendulum (one thread) the following general formulas apply:

$$T^2 = 4\pi^2 \frac{I_b}{D} = 4\pi^2 \frac{I_b}{M/\alpha} \tag{1}$$

$$M = G \cdot I_t \cdot (\alpha/L) \tag{2}$$

From (1) and (2) we obtain

$$T^2 = 4\pi^2 (I_b L)/(I_t \cdot G) \tag{3}$$

$$G = 4\pi^2 (1/T^2) \cdot (I_b \cdot L/I_t) \tag{4}$$

Together, the two threads of the compound pendulum give a restoring torque equal to the sum of the torque from each of them.

$$M_3 = M_1 + M_2 \tag{5}$$

The subscript 1 refers to the upper thread, 2 to the lower one, and 3 to the compound pendulum.

$$D_3 = (M_3/\alpha_3) \tag{6}$$

$$T_3^2 = 4\pi^2 (I_b/D_3) \tag{7}$$

We are interested in the rigidity modulus of the lower thread, i.e., G_2. By combining equations (6), (5), (2), and (7) we get

$$D_3 = D_1 + G_2 (I_t)_2 / L_2 = 4\pi^2 I_b / T_3^2$$

$$G_2 = 4\pi^2 \frac{I_b}{(I_t)_2} L_2 \left(\frac{1}{T_3^2} - \frac{D_1}{4\pi^2 I_b} \right) \tag{8}$$

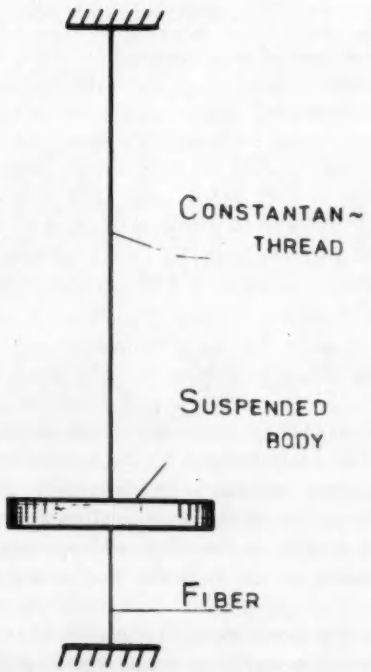

Fig. 1. Principal parts of the combined torsion pendulum.

For a particular suspended body and upper thread, I_b and D_1 are given and can be considered as constants of the apparatus. These constants can be calculated if the shape and density of the body and the torsional rigidity of the thread are known. They can also be measured experimentally by determining the period of oscillation for the simple pendulum (without the lower thread). Combining equations (1) and (8) we get

$$G_2 = 4\pi^2 \frac{I_b L_2}{(I_t)_2}\left[\frac{1}{T_3^2} - \frac{1}{T_1^2}\right] \tag{9}$$

When the lower thread consists of a fiber with circular cross-section,

$$(I_t)_2 = \pi r_2^4/2,$$

which gives

$$G_2 = 8\pi I_b \frac{L_2}{r_2^4}\left(\frac{1}{T_3^2} - \frac{1}{T_1^2}\right) \tag{10}$$

Here I_b and T_1 are constants.

Meredith [5] has calculated and experimentally determined the shape factor ϵ for different fiber cross-sections. The polar moment of inertia $(I_t)_2$ is connected with ϵ by the following equation:

$$\epsilon \simeq s^2/2\pi I_t$$

where s = area of cross-section.

For absolute determinations of the rigidity modulus of fibers with noncircular cross-sections, the reader is referred to Meredith's paper [5]. In the present investigation we were mainly interested in comparing a fiber before and after a treatment. Denoting the original modulus by G_2' and the modulus after a treatment by G_2'', the time of oscillation before treatment with T_3' and after treatment with T_3'', we obtain, from equation (10),

$$\frac{G_2'}{G_2''} = \frac{(1/T_3')^2 - (1/T_1)^2}{(1/T_3'')^2 - (1/T_1)^2} = \frac{(T_1/T_3')^2 - 1}{(T_1/T_3'')^2 - 1} \tag{11}$$

Equation (11) is valid if the length and radius of the fiber are not changed by the treatment. It is therefore not necessary to determine the fiber dimensions. As the radius, r, is often not constant over the length of the fiber and appears in the fourth power in the formula, this is a great advantage.

If the treatment does change the fiber dimensions, the ratio of the torsional rigidities $(G_2' \cdot I_t'/G_2'' \cdot I_t'')$ before and after the treatment can be obtained without determination of the fiber diameter. The following equation is valid:

$$\frac{G_2' I_t'}{G_2'' I_t''} = \frac{L_2'}{L_2''} \frac{(T_1/T_3')^2 - 1}{(T_1/T_3'')^2 - 1} \tag{12}$$

Contrary to the fiber diameter, the fiber length is easy to determine experimentally.

Description

The requirement that it should be possible to perform measurements with the apparatus on a fiber both before and after treatment has influenced the design. As it was considered inconvenient to treat the fiber while clamped in the instrument, it was necessary to ensure that the fiber was always clamped at exactly the same sections. To achieve this and to simplify the handling of the fiber, small plates of perspex (an acrylic resin) were cemented

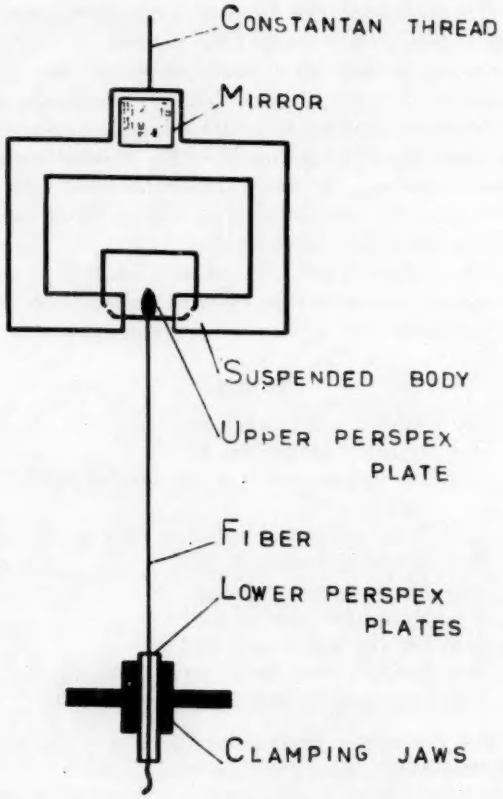

Fig. 2. Schematic drawing of the suspended body and the fastening of the fiber in the apparatus.

to it. At the upper end one plate was used; at the lower end the fiber was placed between two plates. This latter arrangement was adopted to ensure symmetry when the fiber was suspended in the upper plate. This was attached to the suspended body in such a way that the fiber axis coincided with that of the upper thread. Care was taken that the fiber was glued along the middle lines of the surfaces of the plates. These lines were made visible by scratches.

The inertia body was suspended by a constantan thread (60% Cu, 40% Ni) of 0.026 mm diameter and approximately 320 mm length. The rigidity modulus for constantan is about $6 \cdot 10^{11}$ d/cm^2. The dimensions of the thread were chosen to give a period of oscillation of about 15 sec with the suspended body used. The dimensions could be chosen with due regard to the suspension of the test fiber. The suspended body was made of perspex; its design is seen from Figures 2 and 3. The single perspex plate fits in two slots in the body and can easily and accurately be placed there with a pair of tweezers. The moment of inertia of the body was measured and found to be 5.52×10^{-4} d cm sec^2. With a special device the suspended body can easily be held fixed and the upper thread released when changing fibers. A special arrangement was necessary for fastening the lower end of the fiber so that the equilibrium position of the fiber when hanging from the upper end was not changed by twisting, bending, or stretching. The double perspex plates on the lower end of the fiber were to be clamped by two jaws parallel to the plates. The clamping jaws thus had to be movable up and down (for fibers of different lengths) and around the fiber axis as well as perpendicular to the perspex plates. The latter movement must be made individually for the two jaws to avoid deviations in the equilibrium position of the fiber axis.

The whole pendulum system was placed in a perspex casing. The constantan thread was suspended from the top of this casing. The attachment was made in such a way that the thread could be turned by a knob outside the casing and the system thus set in oscillation. The casing was also necessary to protect the oscillating system from air currents and changes in humidity. The rigidity modulus is sensitive to changes in the relative humidity of the air and even the fairly small oscillations of humidity (±2% R.H.) that are normal in a room with controlled humidity are noticeable.

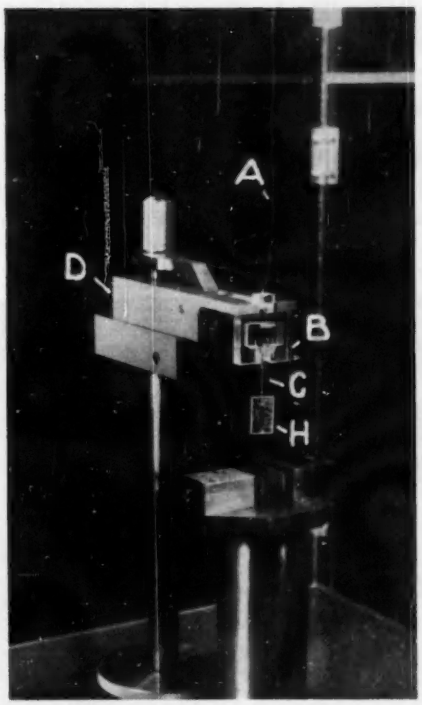

Fig. 3. Detail of the combined pendulum. *A*, constantan thread. *B*, suspended body. *C*, fiber. *D*, device for releasing the upper thread. *H*, lower perspex plates. For the sake of clearness *A* and *C* are drawn thicker than the corresponding fibers.

With the fiber enclosed in the casing, temporary changes in the humidity of the room are damped. Small changes in the mean of the relative humidity can be corrected for by a special arrangement. In the same casing was suspended another torsion pendulum consisting of a fiber of the same material under test and an inertia cylinder. This pendulum was of the one-thread type, as in this case no account had to be taken of the possible effect of loading the fiber. The same fiber was used all the time, and the period of oscillation vs. the relative humidity was measured once. During the measurements on the fibers to be tested, the comparison pendulum was in operation at the same time. Corrections were made on the assumption that the rigidity modulus of the test fiber and the comparison fiber are affected to the same degree by changes in relative humidity. When small changes in fiber properties owing to a treatment were to be detected and the comparative measurements were performed

at large time intervals, this possibility of correcting for humidity changes was especially valuable.

The whole apparatus is shown in Figure 4.

Procedure

Operation

When measurements were to be made on a fiber, it was first glued to the perspex plates as previously described. The single plate was placed in the suspended body and fastened there. If desirable, the fiber could be loaded by hanging a weight from the short free end of the fiber that protruded from the two lower perspex plates. The body was released, and after the system had attained equilibrium the jaws of the lower clamp were set parallel to the plates and moved inward, so that they just touched them. The precision of the measurements was found to be higher if the plates were clamped with a minimum of force. The system was set oscillating by turning the knob on the top of the casing 10–30° and then immediately restoring it to the original position. The comparison fiber was set oscillating in the same way. The period of oscillation was measured with a stopwatch. The fiber length was determined by means of a traveling microscope in front of the casing.

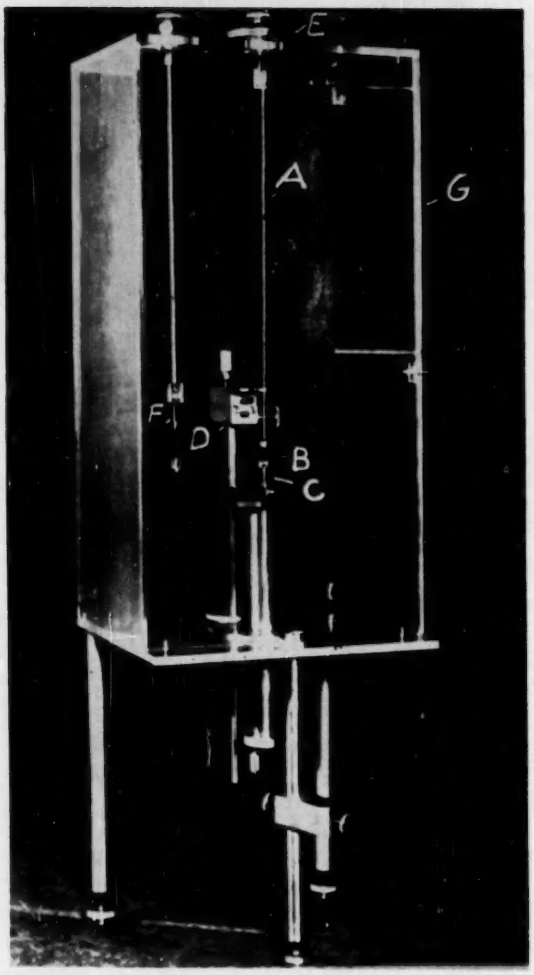

Fig. 4. The combined torsion pendulum. *A*, constantan thread. *B*, suspended body. *C*, fiber. *D*, device for releasing the upper thread. *E*, knob for setting the system in oscillations. *F*, comparison pendulum for corrections of small changes in relative humidity. *G*, perspex casing. For the sake of clearness *A*, *C*, and *F* are drawn thicker than the corresponding fibers.

The analysis of variance of Table III shows that the mean square for "between groups of 3" is significantly greater than the mean square for "within groups of 3." This means that imperfections in the clamping of the lower perspex plates increased the amplitude of the measuring errors. An estimation of the magnitude of the variance components is included in Table III. The component S_w^2, corresponding to the setting of the system in oscillations, is about three times as large as the component S_b^2, corresponding to imperfections in the clamping of the lower perspex plate.

This estimation can be used to determine the suitable number of measurements "within clamping," k, for each reclamping of the lower perspex plate.

It has been shown [2] that the value of k to achieve minimum testing cost for a fixed precision in the estimate of the mean is given by the equation

$$k = \frac{S_w}{S_b}\sqrt{\frac{c_1}{c_2}}$$

where

S_w = Standard deviation "within clamping"
S_b = Standard deviation "between clamping"
c_1 = Cost for reclamping the lower perspex plate
c_2 = Cost for one test, "within clamping"

In the above case cost is equivalent to time. c_1 is estimated to be about twice as large as c_2, which gives a value of $k \simeq \sqrt{3} \cdot \sqrt{2} \simeq 2.5$.

The measurements were therefore performed in the following way. The system was set in oscillation, and the period of oscillation for 5 oscillations

was determined (="one test within clamping"). This was made 3 times. After that, the lower perspex plate was reclamped and the whole procedure repeated.

Effect of Chemical Treatments on the Modulus of Rigidity of Wool Fibers

It was considered interesting to perform torsion experiments on wool fibers from one of the fabrics used in the crease-recovery experiments mentioned in the introduction. The fabric chosen was a plain worsted gray fabric with a weight of 4.6 oz/yd² (156 g/m²). The fabric was extracted with ethyl ether twice (30 and 15 min, respectively), washed in lauryl sulfate (1 g/l at 40°C for 10 min), rinsed, and dried. Thirty warp threads about 20 cm in length were taken from the fabric and untwisted, and six fibers drawn from each thread.

Zero fibers. The fibers were cemented to small perspex plates as described before. To obtain a defined starting condition for the fibers which were to be used to determine the effect of alcoholic potash, they were treated in ethanol (95% for 5 min) and then rinsed in distilled water (3 baths, 5 min in the first). The fibers used for the experiments with sodium hydroxide in butanol kerosene were first laid in butanol (5 min), then in ethanol (3 baths), and finally rinsed in distilled water (3 baths). All fibers were conditioned at 65% R.H. from the wet side.

These fibers are in the following called zero fibers.

Reproducibility of the Measurements

In order to obtain an estimate of the reproducibility of the measurements, the change in the rigidity modulus was determined for the zero fibers after a further treatment in ethanol and water. The results are given in Table I together with an analysis of variance.

From Table I it may be seen that the treatment in water does not produce changes in the period of oscillation greater than those caused by the error of measurement.

Treatment with Alcoholic Potash

An alcoholic potash solution containing 1.8% KOH in 97% ethanol was made by solving 6 g KOH in 195 g absolute ethanol and 5 g water. The solution was filtered through a dry filter and calibrated against sulfuric acid. The zero fibers were placed in the solution for a certain period and then neutralized in sulfuric acid (1% H_2SO_4 in ethanol) and rinsed in 3 baths of ethanol and 3 baths of distilled water. Two periods of treatments were used, 10 min and 30 min. The time of neutralization was 5 min. For all rinsings where several baths were used the time in the first bath was always 5 min and in each of the following 2–3 min.

Before the measurements, the fibers were conditioned overnight at 65% R.H. (from the wet state).

During the treatments the fiber was protected against mechanical damage by two thick nylon filaments cemented to the perspex plates, one on each side of the fiber and somewhat shorter than it (see Figure 5).

The oscillation time was determined both before and after the treatments in alcoholic potash.

The experimental results together with an analysis of variance are given in Table II.

The interaction between treatments and fibers is highly significant. This means that the alcoholic potash does change the torsional rigidity of different fibers to different extents or, in other words, the sensitivity of the method is high enough to detect differences between the fibers. From Table II it is further seen that the mean square for "treatments"

TABLE I. Treatment of Wool Fibers in Ethanol and Water

(The two values are obtained after reclamping the lower perspex plate.)

Fiber	Period of Oscillation in Seconds (Mean values of 15 oscillations, 3×5)			
	Before Treatment		After Treatment	
1	14.73	14.75	14.73	14.75
2	13.94	13.99	13.90	14.00
3	12.49	12.56	12.55	12.52
4	11.83	11.80	11.88	11.86
5	15.47	15.45	15.44	15.44
6	14.32	14.21	14.20	14.26
7	13.20	13.08	13.05	13.11
8	12.41	12.37	12.37	12.29
9	12.59	12.67	12.60	12.61

Analysis of Variance

Source of Variation	Sums of Squares	Degrees of Freedom	Mean Squares	Variance Ratio
Between fibers	47.9226	8		
Between treatments	0.0025	1	0.0025	1.45
Interaction	0.0103	8	0.0013	<1
Between groups of 2	47.9354	17		
Within groups of 2	0.0345	18	0.0019	
Total	47.9699	35		

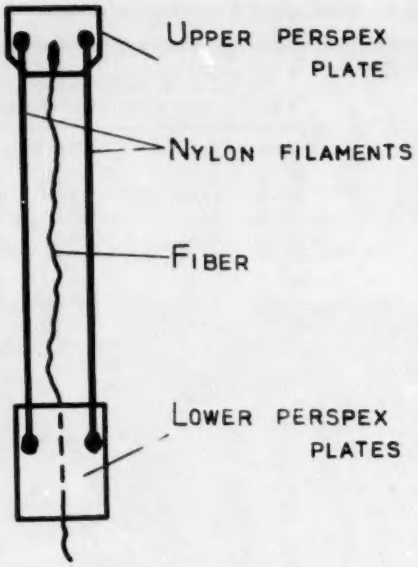

Fig. 5. Arrangement for protecting fibers against mechanical damage during treatments in different solutions.

is significantly greater than the "interaction." The alcoholic potash has thus had an effect on the torsional modulus of the wool fibers. When the difference between the mean values of the oscillation time for one fiber before and after the treatment is larger than or equal to a certain critical difference, d, the treatment has had a real effect on the torsional rigidity. A calculation of d from the values of Table II gives $d = 0.12$. (The calculation is given in the table.) This means that of 13 fibers tested, 9 are changed by the treatment while 4 are unchanged. An increase in oscillation time (decrease of torsional rigidity) is obtained for 11 fibers, and a decrease for 2.

The ratio between the rigidity modulus after and before the treatment is $G_2''/G_2' = 0.90$, calculated from equation (11).

The same analysis has been applied to the values obtained after treatment with alcoholic potash for 30 min. Both "interaction" and "treatment" are significant as before. The mean value of G_2''/G_2' for 15 fibers is 0.91.

The results can be summarized as follows: The treatment with alcoholic potash (2% in 97% ethanol) decreases the modulus of rigidity of wool fibers by 10%. The decrease is the same whether the fiber is in contact with the alcoholic potash for 10 or 30 min.

Treatment with Sodium Hydroxide in Butanol Kerosene

A solution of 6% sodium hydroxide in *n*-butanol was made by boiling 2.46 g NaOH in 41 *n*-butanol (50 ml) under reflux for ½ hr. This solution was diluted with 450 ml kerosene and filtered through a dry filter. The filtrate contained 0.6% by weight of sodium hydroxide.

The fibers were placed in this solution for 30 min, neutralized in 1% sulfuric acid in butanol, and rinsed in butanol, ethanol, and distilled water (3 baths of each).

The oscillation time was determined before and after the treatment. The results are given in Table III together with an analysis of variance. As seen from the latter, the interaction is still significant, but not the effect of the treatment. The critical difference, d, is 0.11, which means that 11 fibers

TABLE II. Treatment of Wool Fibers in 2% KOH in Ethanol for 10 Min

(The two values are obtained after reclamping the lower perspex plate.)

	Period of Oscillation in Seconds (Mean values of 15 oscillations, 3×5)			
Fiber	Before Treatment		After Treatment	
1	15.26	15.24	15.41	15.33
2	15.61	15.51	15.49	15.53
3	14.16	14.24	14.44	14.47
4	12.89	12.85	13.40	13.29
5	13.75	13.76	14.03	13.96
6	11.19	11.24	11.31	11.29
7	13.75	13.71	13.89	13.84
8	14.97	15.02	15.13	15.21
9	12.19	12.07	12.04	11.93
10	10.72	10.73	10.79	10.85
11	13.89	13.65	14.60	14.69
12	14.22	14.15	14.29	14.25
13	13.63	13.64	14.29	14.20

Analysis of Variance

Source of Variation	Sum of Squares	Degree of Freedom	Mean Square	Variance Ratio
Between fibers	105.8198	12		
Between treatments	0.6717	1	0.672	8.72**
Interaction	0.9245	12	0.0770	23.4 ***
Between groups of 2	107.4160	25		
Within groups of 2	0.0855	26	0.00329	
Total	107.5015	51		

The critical interval, $d = \frac{t\sigma \cdot \sqrt{2}}{\sqrt{n}} = \frac{2.06\sqrt{32.9}\sqrt{2}}{100\sqrt{2}} = 0.118.$

In this and subsequent tables the asterisks *, **, and *** are used to indicate statistical significance at the 95%, 99%, and 99.9% levels, respectively.

were unchanged while 5 fibers were affected by the treatment. Of these 5 fibers, 2 became stiffer (decrease in vibration time) and 3 became less stiff. The mean value of G_2''/G_2' is 1.01 for all 16 fibers.

The different effects on the rigidity modulus of the two alkaline solutions are very probably accounted for by the magnitude of the solvent molecules. Speakman [6] has found that alcohols of higher molecular weight than *n*-propyl are unable to penetrate wool fibers. It has subsequently been stated by King [3] that this is a rate effect. Under the experimental conditions of this investigation, the butanol-kerosene solution does not diffuse into the fiber.

TABLE III. Treatment of Wool in 0.6% NaOH in Butanol Kerosene for 30 Min.

Fiber	Period of Oscillation in Seconds (Mean value of 5 oscillations)					
	Before Treatment			After Treatment		
1	15.74	15.56	15.60	15.56	15.68	15.54
	15.72	15.66	15.54	15.72	15.54	15.60
2	14.68	14.64	14.66	14.60	14.68	14.64
	14.80	14.76	14.76	14.64	14.70	14.64
3	15.98	15.92	16.08	15.84	15.96	15.90
	16.04	16.08	16.00	15.90	15.94	16.02
4	13.72	13.60	13.68	13.52	13.60	13.64
	13.70	13.56	13.74	13.52	13.56	13.68
5	11.96	12.08	11.98	11.84	11.86	12.00
	12.14	12.16	12.00	12.00	11.88	12.02
6	15.04	14.96	14.90	14.90	14.96	15.06
	15.08	15.04	15.02	15.08	15.04	14.98
7	15.48	15.52	15.36	15.44	15.56	15.60
	15.56	15.44	15.58	15.40	15.50	15.52
8	15.58	15.70	15.52	15.70	15.72	15.64
	15.48	15.52	15.50	15.74	15.60	15.66
9	15.48	15.60	15.40	15.26	15.42	15.36
	15.28	15.48	15.40	15.32	15.34	15.36
10	14.86	14.72	14.64	14.86	14.90	14.84
	14.64	14.68	14.58	14.84	14.76	14.72
11	15.26	15.36	15.34	15.38	15.26	15.24
	15.40	15.36	15.34	15.24	15.40	15.28
12	14.40	14.52	14.56	14.46	14.40	14.48
	14.54	14.40	14.50	14.44	14.50	14.56
13	15.90	15.96	15.74	16.04	16.08	16.00
	15.64	15.72	15.70	15.88	15.84	15.92
14	14.04	14.16	14.08	14.38	14.34	14.36
	14.10	14.04	14.06	14.20	14.28	14.16
15	15.24	15.26	15.20	15.26	15.20	15.24
	15.28	15.22	15.26	15.24	15.30	15.20

(All experimental values are included in this table. For each fiber the 3 values on the same row are obtained after setting the system in oscillation 3 times without reclamping. The values on the row below are obtained after reclamping the lower perspex plate.)

TABLE III. (Continued)

Analysis of Variance

Source of Variation	Sum of Squares	Degree of Freedom	Mean Square	Variance Ratio	Variance Components
Between fibers	178.1225	14			
Between treatments	0.0028	1	0.0028	<1	
Interaction	0.4652	14	0.0332	3.3**	
Between groups of 6	178.5905	29			
Within groups of 6					
Between groups of 3	0.2689	30	0.00896	2.3**	$3S_b^2+S_w^2$
Within groups of 3	0.5317	120	0.00443		S_w^2
Total	179.3911	179			

S_b^2 = Variance between groups of 3 (caused by the imperfections of clamping the lower end of the fiber).

S_w^2 = Variance within groups of 3 (caused by setting the system in oscillations).

$S_b^2 = 0.00151$; $S_w^2 = 0.00443$.

The variance of the mean value for each fiber

$$= \left(S_b^2 + \frac{S_w^2}{3}\right)/n = 0.00299/n.$$

The critical interval $d = t\sqrt{\frac{(S_b^2 + S_w^2/3)\cdot 2}{n}} = 0.111.$

Acknowledgments

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A Study of the Alcoholysis of Cellulose[1]

Richard B. Valley[2]

Abstract

A study was made of the alcoholysis of cotton linters using methanol, *n*-butanol, *n*-hexanol, and *n*-octanol acidified with hydrogen chloride. All traces of water could not be removed from this system, and further water was formed during the degradations by a reaction between the alcohol and the hydrogen chloride. The linters were degraded in all of the alcohols studied. The amount of linters solubilized during the degradations tended to increase as the molecular weight of the alcohol used increased. It appeared that, in the study made, the cellulose was being degraded by hydrolysis caused by the traces of water present. The acidified alcohols combined with the reducing groups formed to give a degraded cellulose with a low reducing value. The residual reducing power was lowest when methanol was used.

A MEASURE of the availability of portions of cellulose to other molecules is defined as the accessibility of cellulose. Previous workers have shown evidence that the accessibility of cellulose in heterogeneous reaction is partly a function of the size of the molecules penetrating the cellulose.

Molecular-Size Effects in Heterogeneous Reactions

Davis, Barry, Peterson, and King [5] found that methyl, ethyl, and propylamine would swell cellulose directly. Only after preswelling with either liquid ammonia or ethylamine could straight-chain amines as large as heptylamine swell cellulose.

Assaf, Haas, and Purves [1] studied the variation of the accessible portion of cellulose with the molecular weight of the solvent used to carry a reacting molecule into the cellulose. Thallous ethylate, the reacting molecule, formed a thallium alcoholate compound with the accessible cellulose. The alcoholate was then decomposed with methyl iodide replacing the thallium atom with a methoxyl group, and the methoxyl content of the cellulose gave a measure of the accessibility of the cellulose to the solvent used. Complete methylation (45.59%) was considered to represent complete accessibility. The results were plotted as the percentage of methoxyl introduced vs. the molecular volume of the solvent (molecular weight divided by density). An alkali-swollen cotton sample was about 7% accessible to ethyl ether and only about 2% accessible to amyl ether. The same sample was about 5% accessible to ethanol and only about 1% accessible to *n*-heptanol. The curves for ethers and alcohols extrapolated to the same value of methoxyl content at zero molecular volume.

Walseth [19] found that enzyme-catalyzed hydrolysis was characterized by a smaller drop in the average D.P. of the residue compared to an acid-catalyzed hydrolysis of the same cellulose. Walseth believed that enzyme hydrolysis attacked only a small portion of the noncrystalline cellulose but broke the portion attacked into soluble fragments. He contrasted this behavior to that in acid-catalyzed hydrolysis in which the hydrolysis proceeded throughout the entire noncrystalline region, producing insoluble low molecular-weight fragments. Blum and Stahl [3], using a different enzyme, also found that the average D.P. of the residue was lowered only slightly in enzyme-catalyzed hydrolysis. The molecular weights of the enzymes used in both studies were unknown. Enzymes are protein molecules of considerable size, however, and it appears that much of the cellulose was inaccessible to such a large molecule [19].

Hartler and Samuelson [8] studied the hydrolysis of wood cellulose using sulfuric acid and lignosulfonic acid as the catalysts. Degradation of the cellulose, measured by the viscosity of the residues, was more rapid when using sulfuric acid than when ligno-

[1] A portion of a thesis submitted in partial fulfillment of the requirements of The Institute of Paper Chemistry for the Degree of Doctor of Philosophy, Lawrence College, 1955. This work was done under the direction of Kyle Ward, Jr.

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sulfonic acid was used. At the same degree of degradation, the losses were lower when sulfuric acid was used as the catalyst. The authors suggested that during the early stages of the degradation the larger molecular size of the lignosulfonic acid catalyst caused the differences observed.

Weaver, Mackenzie, and Shirley [21] studied the alkylation of cellulose using the straight-chain esters of *p*-toluenesulfonic acid. Under similar reaction conditions, almost complete methoxylation could be obtained in 2 hr while only partial ethoxylation could be attained in 7 hr. A slight reaction occurred with the propyl ethyl ester after 15 hr. No reaction occurred with any of the higher esters. The differences in the rates of reaction were attributed to differences in reactivities of the various esters. On the other hand, the decrease in the maximum amount of alkylation attained as the size of the alkyl group increased indicated a partial influence of molecular size on the course of the reaction.

An estimate of the accessibility of cellulose to molecules other than those discussed in this review was made by the present writer by comparing the size of spaces measured within the cellulose to the sizes of the molecules discussed in the reviews. The spaces within and around the cellulose microfibrils have been measured by depositing colloidal gold and silver within the spaces. Frey-Wyssling [6], using X-rays, determined the size of the gold and silver particles to be 50 to 135 A long and about 10 A wide. He stated that two capillary systems were present: those within the microfibrils and around the micelles (about 10 A wide) and those between the microfibrils (about 100 A wide). Using X-rays, Wardrop [20] found the particle size of precipitated gold to be 73 to 122 A. The sizes of the molecules mentioned in this review were determined by the present writer using Fisher-Hirschfeld-Taylor atomic models and are given in Table I. The sizes used in these models are the collision diameters of the molecules at low velocities.

If only collision diameters are considered, then any capillary (about 100 A wide) between the microfibrils should be accessible to the molecules listed in Table I. The spaces (about 10 A wide) within the microfibrils are of the same order of magnitude as *n*-butanol, *n*-butylamine, and diethyl ether. The relation between size and experimentally determined accessibility is good for *n*-butanol (see Assaf, Haas, and Purves [1]) and butylamine (see Davis, Barry, Peterson, and King [5]). Cellulose is apparently more accessible to ethyl ether [1] than it should be, judging from the molecular size. This may be a result of differences in the functional groups in these compounds.

Alcoholysis

A promising approach for studying the variation of accessibility appeared to be that of alcoholytic degradation. Alcoholysis was considered to be an acid-catalyzed reaction in which the 1–4 links in the cellulose molecule were split by the alcohol. If such a mechanism were correct, then alcoholysis using a series of homologous alcohols could be used to determine the variation of the accessibility of the cellulose with the size of the alcohols. The reactions would be carried out in as nearly anhydrous a medium as feasible to minimize hydrolytic side reactions.

Reeves and coworkers studied the heterogeneous alcoholysis of cellulose in some detail. In 1946, Reeves, Schwartz, and Giddens [9] studied the heterogeneous degradation of cellulose at 20°C. using 0.5 *N* hydrogen chloride in methanol, ethanol, water, and 10% water in methanol. The authors stated that, under the same conditions of temperature and acid concentration, methanolysis and ethanolysis degraded cellulose much more rapidly than did hydrolysis. The addition of water to methanol decreased the rate of degradation markedly. They stated that methanolyzed cellulose differs from hydrolyzed cellulose in being nonreducing, as indicated by the copper number determination, in stability to hot aqueous alkali, and in containing acid-labile alcohol residues. They found under more severe

TABLE I. Molecular Sizes Using Fisher-Hirschfeld-Taylor Atomic Models

Molecule	Extended Length (A)	Width (A)
Methanol	5	4
Ethanol	6.5	4
n-Butanol	9	5
n-Heptanol	10.5	5
Methylamine	5.5	4.5
Propylamine	7.5	5
n-Butylamine	8	5
Diethyl ether	9	4.5
Diamyl ether	17.5	6.5
Hydronium ion (H_3O^+)	4	2.5
Ammonia (NH_3)	4	4

conditions that the same limiting fluidity would be reached in both methanolysis and hydrolysis. The methanolyzed samples had higher methoxyl contents (0.58% for a methanolyzed native cellulose compared to a normal value of 0.25% before methanolysis) which could be decreased by refluxing for 24 hr in 0.5 *N* hydrochloric acid. The authors believed that the glucose-glucose links in the original cellulose were split by the acid-catalyzed alcohol with the simultaneous introduction of an alcohol residue on the cellulose molecule. Reeves [13] in a patent reported the alcoholysis of cotton with several other alcohols at 120°C. The results are listed in Table II. In every instance the residue was discolored. He also stated that either sulfuric or *p*-toluenesulfonic acid could be used as the catalyst. The recommended upper limit of catalyst concentration was 2 normal.

Mehta and Pacsu [10] and Pacsu [12] studied the heterogeneous methanolysis of cotton and rayon at 0°C, using 9.42 *N* hydrogen chloride as a catalyst. The results were similar to those found by Reeves and coworkers. The limiting D.P. for the cotton was found to be 250.

Blair [2] studied the alcoholysis of several cotton samples using 2-methoxyethanol and *p*-toluenesulfonic acid. The temperature range covered 90 to 110° C and the concentration of catalyst varied from 0.15 to 1.0 *N*.

In 1954, Sharkov, Korol'kov, and Krupnova [16] in a Russian journal reported the methanolysis and ethanolysis of cotton using sulfuric acid as the catalyst. The rate of degradation was found to increase with an increase in the alcohol concentration in the acid-alcohol-water system, the addition of a nonpolar solvent to the solvent system, and an increase in the available surface of the cellulose. An important statement was made in the abstract: "The nature of cleavage is analogous to that observed in hydrolysis."

TABLE II. Alcoholysis of Cotton with Higher Alcohols

(Temperature: 120° C)

Alcohol	Concentration of HCL (*N*)	Time (min)	Fluidity in Cuam (rhes)	Loss of Weight (%)
n-Propanol	0.11	30	17.9	6.0
	0.22	30	19.2	9.0
	0.44	60	23.0	18.0
n-Butanol	0.11	30	17.9	2.0
	0.44	60	18.9	16.0
	0.44	240	23.9	16.5
n-Pentanol	0.44	60	22.2	19.0

Materials

Cotton Linters

The linters used in this work were bulk cotton linters of D.P. 1200 obtained from the Buckeye Cotton Oil Company. The linters were air dry and were rewet by soaking for 48 hr. The linters were slurried in small batches, centrifuged, and disintegrated in the pulp disintegrator. After disintegration, the pulp was thoroughly mixed, placed in several polyethylene bags, and stored at 5–10°C. The average oven-dry solids content was 46.6%. Extractable material, ash, copper number, and intrinsic viscosity were determined on linter samples dehydrated by washing with methanol, acetone, and ether, followed by air drying. The values are given in Table III.

Organic Liquids

The organic solvents used in the degradation studies were obtained commercially. All reagents were purified by distillation no more than 10 days before using. The methanol and *n*-butanol were distilled at atmospheric pressure using a jacketed Widmer column. The *n*-octanol was distilled at a total pressure of 90 mm mercury in a Vigreux column. The impure *n*-hexanol was refluxed for 24 hr with sodium methoxide in an excess of methanol and then distilled at a total pressure of 50 mm mercury. After distillation, the alcohols were stored over sodium sulfate until used. The tetrahydrofuran was refluxed over sodium for 24 hr and then distilled

TABLE III. Analysis of Undegraded Cotton Linters

Ash at 600° C	0.142%
Copper number	0.156
Intrinsic viscosity in cupriethylenediamine at 30° C	5.08
Successive extractions by	
Ethyl ether	0.193%
95% Ethanol	0.034%
Absolute methanol	0.073%
Total extractives	0.0300%

through the Vigreux column at atmospheric pressure. The distilled product was stored over sodium.

All acidified organic reagents were prepared by bubbling dry hydrogen chloride through approximately 200 ml of the liquid until the desired concentration of acid was exceeded. The acidified reagent was then diluted to the volume needed; the acid concentration was measured; and a final adjustment of the acidity was made.

Standard Experimental Methods

Water Determination by Karl Fisher Reagent

All Karl Fisher determinations were carried out following the general procedure proposed by McKinney and Hall [9]. In this method, an excess of Karl Fisher reagent is added to the unknown and then back-titrated with standard water in methanol. The end point is determined electrometrically, using the dead-stop method. In most cases, it was necessary to dilute liquid samples in a known amount of methanol in order to obtain satisfactory end points. Fiber samples were tested using the method proposed by Mitchell [11], in which the unknown is added to methanol, allowed to stand 1 hr, and then titrated in the standard manner with the fibers still present.

Acidity

The acidity of the alcohols after the introduction of hydrogen chloride was determined by adding an aliquot of the alcohol to water and titrating with base using phenolphthalein as an indicator. All the end points were sharp and easily observed.

Viscosity

The viscosities of all samples were determined at 30°C in cupriethylenediamine solution, following the general procedure outlined by Wetzel, Elliot, and Martin [22]. The intrinsic viscosity of each sample was determined from measurements of the viscosity at four different concentrations.

All samples were dissolved under prepurified nitrogen in the following manner: (a) Air-dry cellulose was weighted by difference into 60-ml serum bottles; (b) an estimate was made of the volume of liquid necessary to give the final concentration needed (0.05 to 0.25 g/100 cc); (c) distilled water equal to one-half of the amount of liquid calculated was added and the serum bottle stoppered with a self-sealing stopper; (d) the air present in the sample was removed by alternately evacuating and filling the bottle with prepurified nitrogen, using the apparatus described by Browning, Sell, and Abel [4]; (e) after the air was flushed from the bottle 1.0 *M* cupriethylenediamine was added to give a final solution which was 0.5 *M* in copper; (f) the sealed bottles were shaken for 1 hr and then placed in the constant temperature bath for at least 1 hr before a sample was removed by hypodermic syringe; and (g) the viscosity was determined at 30°C in Ostwald-Fenske-Cannon pipettes.

Copper Number

Copper numbers were determined on air-dry samples, using a modification of TAPPI Method T 215 m-50. The sample size was reduced to about 0.4 g. The normality of the potassium permanganate solution was also decreased to 0.02 *N* to improve the sensitivity of the titration. A permanganate solution of this strength is not stable for long periods so a solution was made daily by diluting 0.1 *N* stock solution. The diluted solution was standardized against sodium oxalate. It was found that the reproducibility of duplicate samples was improved by titrating to a definite color and then correcting for the excess permanganate solution required by titrating an equal volume of distilled water to the same color.

Total Reducing Sugars

Total reducing sugars were determined by the Somogyi method [17]. The determination was standardized against known concentrations of D-glucose. All values of sugar concentrations were determined on solutions that were 0.5 *M* in sodium chloride. When determining very low sugar concentrations both the blanks and the standard sugar solutions were also made 0.5 *M* in sodium chloride to correct for a small change in rate caused by the presence of the salt.

Oven-Dry Solids

The solids contents of all samples were determined by vacuum-oven drying at 80°C. The temperature was increased over the 40°C often used in order to assist in the removal of the higher boiling alcohols.

Under these conditions, samples were dried to constant weight within 4–5 hr.

Russell, Maass, and Campbell [15] found that as much as 2% of methanol and other alcohols were retained by cellulose on drying alcohol-wet cellulose samples, even at 100° C, under vacuum. All of the samples collected in this work were dried by washing successively with methanol, acetone, and ethyl ether, and then removing the ether by drawing air through the sample. This procedure is hereafter called "solvent drying." The possibility of high solids contents occurring from the entrapment of solvents was tested by determining the solids content of moist linters in two ways: (a) solvent drying followed by vacuum drying at 80°C and (b) vacuum-oven drying at 80°C. The results were 55.6% for solvent drying plus oven drying and 56.3% for vacuum-oven drying. It does not appear that there is any inclusion of organic liquids in cotton samples air-dried from ether.

Experimental Results and Discussion

Preliminary Experiments

One source of water during alcoholysis was the water present on the cellulose. Therefore, the linters were dehydrated as thoroughly as possible before the addition of the alcohol. Direct drying of water-wet cellulose was not used since it was shown by Grotjahn and Hess [7] and Staudinger and Döhle [18] that drying from water decreased the internal surface and the reactivity of cellulose toward organic liquids. In addition, trials using dry fibers indicated that air-dried cellulose was not easily wet by the higher alcohols. The linters were dehydrated by extracting the water with methanol, followed by further extractions with the alcohol to be used. Attempts were made to remove additional water from the linters using azeotropic vacuum distillation and low temperature sublimation. The linters used were dehydrated, using solvent replacement, prior to the additional treatment. Table IV compares the amount of residual water on linters dried by the several methods used. There does not appear to be any advantage gained by additional treatments after solvent replacement.

Another possible source of water during alcoholysis is the formation of water from a reaction between the alcohol and hydrogen chloride. Therefore, changes in the water content for methanol, *n*-butanol, *n*-hexanol, and *n*-octanol acidified with dry hydrogen chloride were measured. The initial acidity was about 0.5 *N* and the temperature was held at 30°C in a constant-temperature water bath. The results are given in Figure 1. Only methanol showed a marked reaction. The other alcohols appeared to be approaching an equilibrium water content.

TABLE IV. Drying of Cellulose: Comparison of Various Methods

Method	Liquid	Water Based on Dry Cellulose (%)
Repeated distillation	*n*-Butanol	0.41
Repeated distillation	*n*-Hexanol	0.31
Sublimation at −10° C	Tetrahydrofuran	0.24
Solvent replacement*	Methanol	0.79
Solvent replacement*	*n*-Butanol	0.40
Solvent replacement*	*n*-Hexanol	0.40
Solvent replacement*	*n*-Octanol	0.32
Solvent replacement*	Tetrahydrofuran	0.78

* Linters were dehydrated with 3 extractions using methanol followed by 3 additional extractions with the liquid listed.

The degradations made in alcohols used a catalyst concentration of only 0.05 *N* in hydrogen chloride, and an estimate of the amount of water formed by the reaction of alcohols and hydrogen chloride was made from the data obtained at an acidity of 0.5 *N* by assuming that the main reaction was: ROH + HCl = RCl + H_2O. The results are given in Table V.

In addition to the two sources of water discussed above, water may enter the system with the alcohols. In the process of purifying the alcohols, the water content was lowered to values which were 50% or-

TABLE V. Alcohol-Acid Reaction

Equilibrium Constants and Water Contents at Equilibrium

$$ROH + HCl = RCl + H_2O$$

$$K = (RCl)(H_2O)/(ROH)(HCl)$$

$$\text{or } K(ROH) = K' = (H_2O)^2/(HCl)$$

Alcohol	K′ at 0.05 *N* HCl	Water Content at Equilibrium, 0.05 *N* HCl (mg/ml)
Methanol	0.401	2.54
n-Butanol	0.0341	0.74
n-Hexanol	0.0121	0.44
n-Octanol	0.0248	0.64

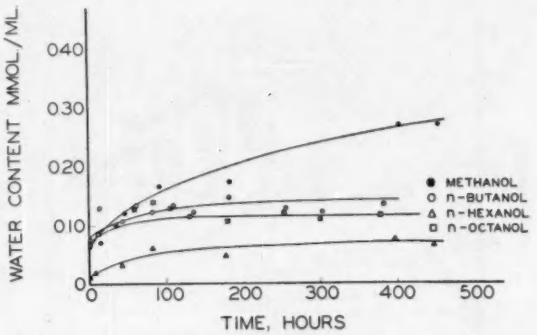

Fig. 1. Changes in water content in alcohols acidified with hydrogen chloride at 30° C.

less of the equilibrium water content of acidified alcohols.

An estimate of the relative importance of the water in the alcohol-cellulose system may be made if it is assumed that an anhydrous alcohol-cellulose system is one in which there is not enough water present to allow for hydrolysis of the cellulose. Based on the weight of cellulose, only 0.033% of water would be necessary to degrade a cellulose sample having a number average D.P. of 800 to a D.P. of 200. If there are 15 g of linters dispersed in 850 ml of alcohol, this amount of water would represent a concentration in the liquid phase of about 0.006 mg/ml. This value is about one-thousandth of the equilibrium water concentration of any of the higher alcohols. Depending on the rapidity at which the water is formed by the alcohol and acid, this low value would be increased. It does not seem possible, therefore, that anhydrous conditions can be maintained in alcohols acidified with hydrogen chloride.

Acid Degradation of Cotton Linters

All degradations were made at 30 ± 0.2°C in a constant-temperature bath. All the studies made on large samples of linters were carried out in 2-l round-bottomed flasks fitted with a glass stirrer running through a mercury seal. The studies made on small samples were carried out in 500-ml round-bottomed flasks fitted with ground-glass stoppers.

Fiber samples taken during the experiments were treated so as to insure that the insoluble material recovered did not contain short-chain fragments soluble in water or methanol but insoluble in a higher alcohol. Two procedures were followed. Hydrolyzed samples were filtered, using suction, washed with distilled water until the filtrate was neutral, and solvent dried. Samples of linters degraded in organic liquids received the following treatment: (a) The filtered linters were redispersed in methanol and the residual acidity neutralized, using sodium hydroxide; (b) additional water was added to methanol to give a final ratio of methanol to water of 5 to 1; and (c) after 24 hr, the sample was again filtered, and solvent dried.

All the original liquors removed with each filtrate were collected and the volume determined. A portion of each liquor sample was set aside for the determination of soluble carbohydrates. The methanol-water extractions of all samples were also collected and treated in the same manner. The soluble carbohydrates were measured by determining the reducing power of the liquors and extraction filtrates after hydrolysis, expressing the value as an equivalent concentration of glucose, and converting the glucose concentration to an equivalent concentration of cellulose.

Properties of Acid-Degraded Linters

Figure 2 shows the variation of the intrinsic viscosities of the degraded linters with time. Degradation of cotton linters occurred in all the acidified liquids used. The rate of degradation in acidified nonaqueous liquids was much greater than the rate of degradation in aqueous acid of the same concentration. The rate of degradation in 2.0 *N* hydro-

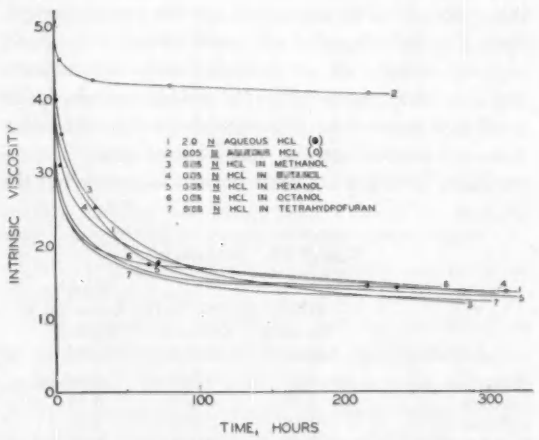

Fig. 2. Intrinsic viscosity vs. time of treatment at 30° C. (The experimental points have been omitted on most curves to improve the clarity.)

chloric acid was about as rapid as the rate of degradation by 0.05 *N* hydrogen chloride in methanol. A rough estimate of the initial rates of degradation in liquids acidified with 0.05 *N* hydrogen chloride was made by comparing the viscosity changes during the first 10 hr of reaction. The values are given in Table VI. The changes, beginning with the smallest, ranked water, methanol, butanol, hexanol, octanol, and tetrahydrofuran. Within the limits of experimental error, there was no difference in the leveling-off viscosity found for 2.0 *N* hydrolysis and any of the nonaqueous liquids used.

Figure 3 shows the variation of the copper number of the degraded linters with the time of treatment. The results found for hydrolysis are normal and show only differences caused by the different acidities used. The values found for degradation in tetrahydrofuran (Study T-1) are similar to those found for hydrolysis except for somewhat lower values at corresponding degrees of degradation. In all degradations carried out in alcoholic media, there was an initial increase in copper number of the residues during the first 24 hr. After this time, the reducing power of the residue either decreased or leveled off and tended to approach a steady value after extended degradation. The steady values found from Figure 3 at 300 hr for the four alcohols were methanol, 0.3; butanol, 0.5; hexanol, 1.2; and octanol, 1.1. The comparative value found by extrapolation for 2.0 *N* hydrolysis was 5.7.

Loss-time curves were calculated from (a) the initial weight of linters added and the samples recovered, (b) the volume of all liquids added or removed, (c) the volume of all methanol-water extractions, and (d) the concentration of soluble carbohydrates in all liquid samples. Figure 4 shows the percentage loss as a function of the time of treatment. Reproducibility between duplicate curves was poor but the losses found represent only very small quantities. It may be that experiments in which the losses were greater would show better agreement.

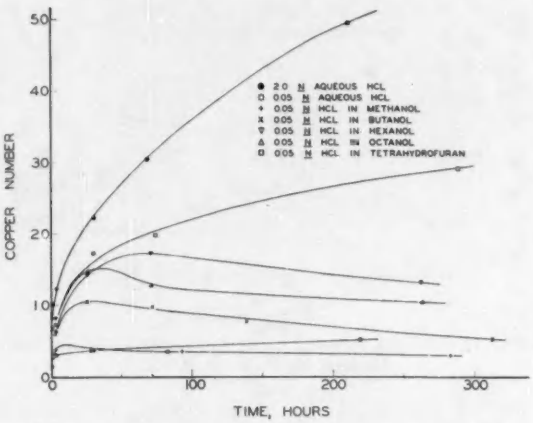

Fig. 3. Copper number vs. time of treatment at 30° C.

The data for soluble cellulose for Study B-1 were very scattered, and duplicate determinations differed by several hundred per cent. It is believed that the scatter was caused by the very small liquor samples (20 to 40 ml) taken in this experiment, as later experiments in which the volumes of liquor taken were about 100 ml showed good agreement. The curve for Study B-1 was not included in Figure 4 for this reason.

The soluble losses were under 1.2% for all of the studies except degradation in tetrahydrofuran. The comparative values at 288 hr are given in Table VI. At constant acidities, degradations in nonaqueous media showed higher losses than did degradations made in aqueous acid. The losses for degradation in methanol were lower than the losses for degradations made in other alcohols. Losses in acidified tetrahydrofuran were much higher.

TABLE VI. Summary

Liquid	10-Hr Viscosity Change*	Acid Sorbed by Cellulose (meq/g)	Soluble Losses at 288 hr† (%)
Water	0.67	0.052	0.05
Methanol	1.79	0.035	0.13
n-Butanol	2.28	0.054	0.75
n-Hexanol	2.63	0.132	0.79
n-Octanol	2.75	0.117	0.80
Tetrahydrofuran	2.76	0.384	4.10

* From Figure 2.
† From Figure 4.

Changes in the Acidity of the Liquid Phase

Mixing cellulose and acidified liquids produced a decrease in the amount of acid titratable in the liquid phase. Mixing changes were measured by determining the acidity of the liquids just before adding them to the cellulose and by determining the acidity of the liquid phase within ½-hr of mixing. A summary of the apparent sorption of acid by the cellulose for all degradations, using 0.05 *N* hydrogen chloride, is given in Table VI. Water, methanol, and butanol produced the smallest sorption while the sorption in

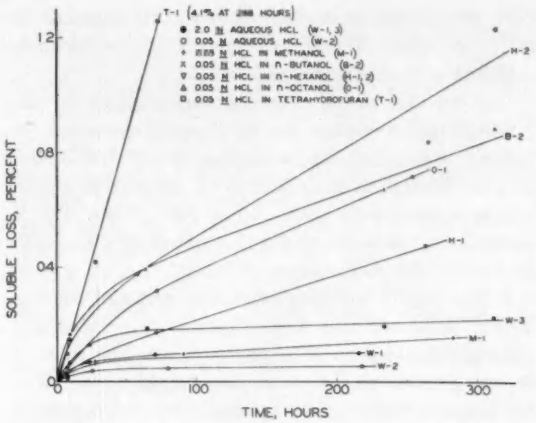

Fig. 4. Soluble losses vs. time of treatment at 30° C.

hexanol and octanol was over twice as high. The amount of acid sorbed from tetrahydrofuran was much higher than from any other liquid acidified with 0.05 *N* hydrogen chloride.

Discussion

Alcoholysis has been stated by Reeves and coworkers [13, 14] to be an unique reaction in which the cellulose molecule is split by acid-catalyzed alcohol with the formation of a nonreducing alkyl glycoside. The work of Assaf, Haas, and Purves [1] indicated that cellulose was almost inaccessible to alcohols larger than butanol. If the mechanism suggested by Reeves occurred in degrading cellulose with acidified alcohols, the differences in the reaction with homologous alcohols should be noted as the molecular weight of the alcohols increased. An increase in the molecular weight of the alcohol should lead to a decrease in the amount of the cellulose solubilized because a smaller portion of the cellulose would be attacked. The viscosity of the residue should be higher because more of the long chains originally present in the cellulose would not be accessible to the larger alcohols.

Cotton linters were degraded in this study with four acidified alcohols: methanol, *n*-butanol, *n*-hexanol, and *n*-octanol. The same leveling-off viscosity was found for all four alcohols. The amount of cellulose solubilized during the degradations was smallest for degradations made in methanol and larger for the other alcohols. Under the mechanism of alcoholysis suggested by Reeves and coworkers, the copper numbers of the residues should decrease slightly during the degradation. This behavior was not observed.

The data which have been presented in this work do not fit the mechanism of alcoholysis in three points. There was no difference in the leveling-off viscosity when different alcohols were used. There was no decrease in the amount of cellulose solubilized as the molecular weight of the alcohol used increased. Finally, changes in the copper numbers of the residues did not indicate that nonreducing groups were formed in one reaction. It does not seem possible, therefore, that alcoholysis occurs in the system studied here.

A new explanation can be suggested. The system in question must of necessity contain traces of water. In such a system, the 1–4 links are split by acid-catalyzed hydrolysis. The reducing groups formed by the hydrolysis then react with the acidified alcohol to form nonreducing groups, probably glycosides. In addition, in such a two-phase system containing acid, the concentration of acid at the cellulose-liquid interface is increased by a sorption of acid by the cellulose. The amount of sorption is dependent on the nature of the liquid phase.

This proposed mechanism agrees with the results of this work in the following points. The same leveling-off viscosity would be reached in every alcohol because the cellulose was actually degraded by hydrolysis. The amounts of cellulose solubilized during the degradation would not decrease as the molecular weight of the alcohols increased but would depend on other factors, which will be discussed later. Finally, the formation of nonreducing groups involves two simultaneous reactions. The increase in the copper number followed by a decrease or leveling off is also typical of two simultaneous reactions. Further, the very slight increase observed when methanol was used indicates that in this case the second reaction was faster than when other alcohols were used. This behavior also agrees with the slightly greater reactivity of methanol compared to the higher alcohols.

The hypothesis developed can be extended to cover the degradation of cellulose by acidified tetrahydrofuran. In this case, the degradation of cellulose proceeded by hydrolysis, but the reducing groups formed were not converted to nonreducing groups in a second reaction. The slight difference between the reducing power of hydrolyzed linters and linters degraded in tetrahydrofuran at similar degrees of

degradation was possibly caused by a secondary oxidation of some of the aldehyde groups.

Support for the hypothesis that increased rates of degradation in nonaqueous media are caused by a preferential sorption of acid by the cellulose is of a general nature. In this work the degradation medium was a two-phase system consisting of cellulose plus sorbed water and acid as the solid phase and the nonaqueous liquid containing water and acid as the liquid phase. In this system there will be a partition between the cellulose and the liquid for the available acid. Cellulose, with three hydroxyl groups on each glucose unit, will be favored in this partition as the polarity of the liquid decreases. The concentration of acid at the interface of the two-phase system will thus depend on the polarity of the liquid. As the acidity increases at the interface, the rate of degradation should increase. The increase would be noted by a more rapid decrease in the viscosity of the residue and in greater soluble losses.

In Table VI the liquids studied are listed in order of decreasing polarity. The viscosity changes agreed in every case with the hypothesis, increasing as the polarity of the liquid decreased. The determination of soluble losses was not as accurate as that of viscosity change. However, losses were least for 0.05 *N* hydrolysis, somewhat higher for acidified methanol, higher for the other three alcohols, and very high for acidified tetrahydrofuran. The values for the sorption of acid by cellulose from the various liquids agreed only partially with the hypothesis. The values measured were very small, however, and the technique used had not been developed to measure such small changes. Cellulose in water, methanol, and butanol showed much smaller sorption values than did cellulose in the other alcohols. Again, the value for sorption from tetrahydrofuran was much higher. These results cannot be said to give definite proof of the hypothesis that increased rates of degradation in nonaqueous media are caused by increased sorption of acid from the liquid. It is believed, however, that there is fair evidence of such a phenomenon.

Alcoholysis of cellulose might still occur if a truly anhydrous system could be maintained throughout the degradation. Such a system seems very difficult, if not impossible, to achieve.

Summary and Conclusions

Techniques were developed for the preparation of alcohols and cellulose samples containing minimum quantities of water. It was not possible to prepare anhydrous materials, nor was it possible to maintain water contents below 0.2% in alcohols acidified with hydrogen chloride.

The alcoholysis of cellulose was studied by degrading cotton linters at 30°C with methanol, *n*-butanol, *n*-hexanol, and *n*-octanol, using 0.05 *N* hydrogen chloride as the catalyst. Comparative degradation studies were made using 0.05 *N* and 2.0 *N* aqueous hydrochloric acid and tetrahydrofuran acidified with 0.05 *N* hydrogen chloride.

It was found that degradation in acidified organic liquids produced the same leveling-off viscosities, although the change in viscosity during the first 10 hr was greater as the molecular weight of the alcohol used increased. The soluble losses were greater for those degradations made in organic liquids. The reducing values of the residues of linters degraded in alcohol showed an increase during the early stages of degradation and then leveled off or decreased. This behavior was in direct contrast to that for hydrolysis, in which the reducing value of the residue increased steadily. The reducing value of the highly degraded residues from the studies made in alcohols were related to the alcohol used. The smaller alcohols gave residues with lower reducing values.

It is believed that alcoholysis as a distinct reaction did not exist under the conditions used in this study. There was no evidence that the accessibility of the cellulose to alcoholysis was a function of the molecular weight of the alcohol. Further, the initial increases in reducing power of the residues argues against such a mechanism.

It is suggested that degradations of cellulose in acidified alcoholic media are actually initiated by traces of water present in the system and that nonreducing cellulose is formed by condensation of the alcohol with the reducing groups formed on hydrolysis of the 1–4 links. It is suggested that the accelerated rates of degradation found in organic liquids are caused by a sorption of acid from the nonaqueous phase by the cellulose so that the effective acidity at the cellulose-liquid interface is much higher than that measured in the liquid phase.

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The Relation of Single-Fiber to Flat-Bundle Strength and Elongation of Cotton

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Abstract

Seven cotton and one rayon samples were tested at various gage lengths, using the Stelometer. A method of estimating the slip length of fibers in a flat-bundle test is derived and applied to these data in order to obtain a "corrected" gage length for use in calculating strain at break.

Also, a method similar to that proposed by Platt et al for calculating the maximum possible bundle tenacity from breaking load and elongation at break of single cotton fibers is applied to previous single-fiber tensile data. The resulting derived values of bundle tenacity and per cent elongation are compared with measurements made on fiber bundles at equivalent gage lengths. The flat-bundle values of tenacity and elongation, measured with the Stelometer, show a good correlation with the values measured on single fibers.

THE importance of measuring the physical properties of fibers which are known to affect product quality or processing characteristics of cotton is recognized by the textile industry. These measurements are of equal importance to the breeder in selecting new strains having desirable fiber characteristics. Several tests have been developed to furnish as accurate a measure of the physical properties of cotton as is consistent with the speed required in providing test results [1]. However, there is a continuing need for improvements in methods of testing and for a better understanding of measurements made by existing methods.

Two different approaches have been employed in determining which physical properties and tests are important. In the first approach, correlation analyses of fiber-test results such as length, strength, fine-

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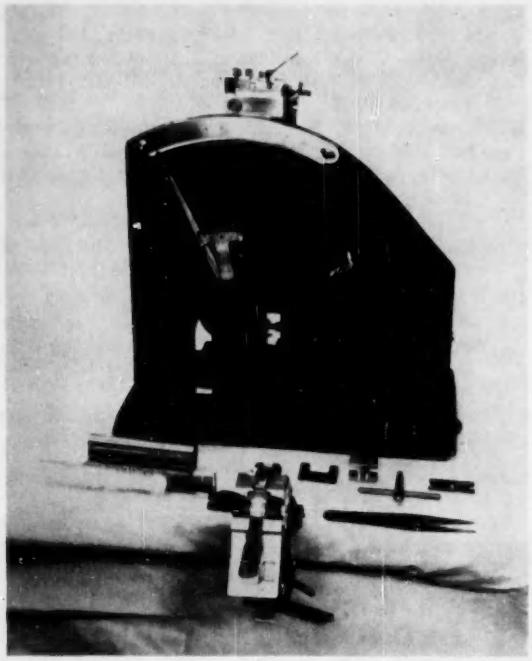

Fig. 1. The Stelometer used for making a flat-bundle test of breaking load and elongation.

ness, and maturity with specific qualities of the end products such as yarn strength, elongation, and appearance have been employed [18]. This approach can be useful even if the tests do not measure a single well-defined physical property but include factors influenced by several individual or combinations of fiber properties.

The second approach consists of analyzing mechanical properties of finished products by stress analysis, in which both the geometry of construction of the yarn and the physical properties of the fibers are considered [13]. Such an analysis requires that measurements of definite physical properties of individual fibers be made under known test conditions or that measurements be made on groups of fibers where the relation of the group measurement to that of individual fiber measurements can be established.

In the first approach, the Pressley [2] flat-bundle and Chandler round-bundle test methods have been used quite successfully to measure strength [15, 16]. These methods measure the breaking load of a bundle of fibers. The bundles are gripped at as short a distance between jaws as possible, but there is a small but finite gage length, the magnitude of which is unknown and variable because of slippage of fibers between the surfaces of leather and steel and between fiber surfaces. Efforts to improve the flat-bundle test have resulted in development of the Clemson flat bundle Tester [2, 3] [2] and the Stelometer [6].[3] The Clemson tester was used in a more recent study of the correlation of yarn strength with bundle strength measured at different gage lengths [2].

The present investigation was undertaken to determine whether bundle strength and elongation when measured with the Stelometer are closely related to the corresponding values measured on single fibers. It will be shown that computed values for both bundle strength and bundle elongation, derived from single-fiber measurements, agree satisfactorily with the observed values obtained from Stelometer tests on bundles. It is therefore concluded that the bundle test with the Stelometer can replace the single-fiber test in many research studies without sacrificing accuracy or significance of the results.

Samples

Seven samples of American-grown commercial cottons whose fibers have a wide range in physical properties and a high tenacity viscose rayon sample were selected. The cotton samples, identified by their varietal names, were S × P, Hopi Acala 50, Acala 1517, Deltapine 14, Stoneville 2B, Coker 100 Wilt, and Rowden 41B. Their physical properties have been given in an earlier report [5]. The rayon sample, obtained by untwisting the filaments of a commercial viscose tire cord, was selected to illustrate the difference between native and synthetic fibers.

Test Methods

All measurements on both single fibers and flat bundles were made in an atmosphere controlled at 70°F and 65% R.H.

Single Fibers

The tenacities, breaking loads, and elongations at break at 7.1-mm gage length and methods of measur-

[2] The mention of trade names does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

[3] An instrument developed at the University of Tennessee under a R. M. A. Contract of the U. S. Department of Agriculture and supervised by Southern Regional Research Laboratory (U. S. Patent Pending).

ing these properties were those reported in previous publications [5, 8, 9]. The 300 fibers tested were selected from the three consecutive length groups of the distribution containing the largest total weight of fibers. The average time required for a fiber to break was about 10 sec.

Flat Bundle

The Stelometer, Figure 1, was used in the present investigation to measure tenacity and elongation for fiber bundles. The instrument was designed to control many variables in techniques common to bundle tests and to measure breaking load and elongation of bundles at various gage lengths. The rate of loading can be controlled at any constant rate desired for the test. In addition, the instrument gives a measure of bundle elongation which is magnified 40 times for precision and ease of reading.

The technique used was that worked out by Hertel [6, 7]. Briefly, the procedure for measuring these properties is as follows. A well-conditioned sample of about 0.5 g is distributed on a pair of Fibrograph combs [2] and combed by the technique recommended in the preparation of a sample for length measurements [1, pp. 317–320]. The projecting tuft of fibers is gripped with a special transfer clamp, *B* of Figure 2, at a distance from the comb teeth slightly greater than the width of the Pressley jaw,[2] and all loose fibers are combed out. The lengths of fibers in the resulting bundle compare favorably with lengths of the modal and two adjacent groups of fibers in the original length distribution [4]. The thin flat bundle, *A* of Figure 2, so prepared is stretched across the Pressley jaws,[2] using the guides of the jaw vise, *C*, to keep the fibers aligned while being pretensioned. A load of about 15 g is put on the bundle by the weight of the transfer clamps, the vise being tilted to 45° for this purpose. This load is equivalent to approximately 0.02 g per fiber, whereas about 0.2 g is necessary to remove kinks from the single fibers. The jaws are closed and the screws tightened until a torque of 8 lb-in. is read from a built-in torque meter. Thus by control of jaw pressure, bundle width, and bundle thickness, the fatigue of leather is reduced and the reproducibility of results is increased.

The time required for a bundle to break at the rate of loading used was about 10 sec, which was comparable to the time required to break the single fibers.

Tenacity was calculated as the ratio of breaking load to linear density of the bundle; the linear density was calculated from the weight of the bundle and its cut length. The assumption was made that the linear density of sections under stress was equal to that of the whole bundle.

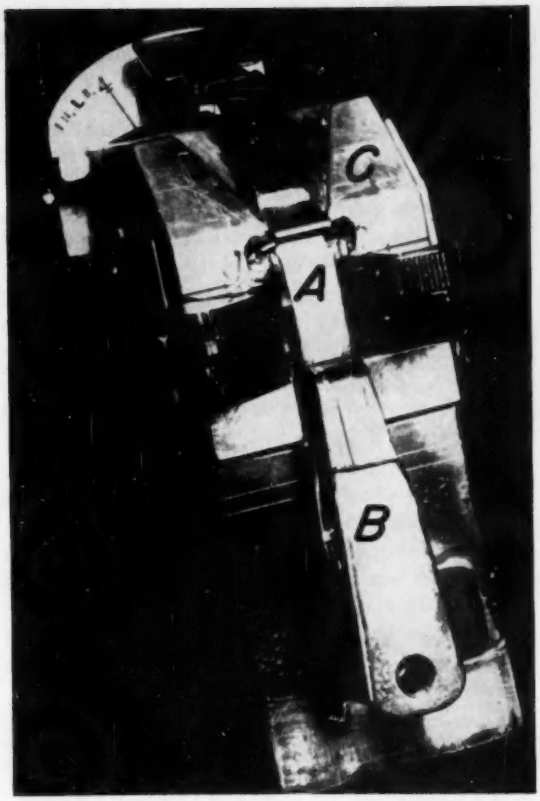

Fig. 2. Specimen, *A*, held in fiber transfer clamp, *B*, and positioned across Pressley jaws located in vise, *C*.

Due to inherent errors in measuring elongation as well as to errors in determining the length of the bundle section under tension, values of strain calculated from the bundles were less accurate than values of tenacity. These errors in measuring elongation arise partly from setting the Stelometer jaw holder to compensate for spacers and partly from variations in dimensions of different jaws. The total extensions involved for 5-mm specimen lengths are of the order of 0.4 to 0.7 mm.

Bundle Slippage

In measuring bundle elongation and in deriving values involving it, the length of specimens under

TABLE I. Mean Single-Fiber and Flat-Bundle Tenacity and Elongation at Break and Calculated Maximum Possible Bundle Tenacity and Elongation at Maximum Load for Specimens Measured or Computed to 7-mm Gage Length

	Mean Single Fiber		Bundle			
			Experimental		Calculated Maximum	
Sample	Tenacity (g/gx)	Elongation (%)	Tenacity (g/gx)	Elongation (%)	Tenacity (g/gx)	Elongation (%)
S × P	4.9	13.7	2.02	10.0	3.14	11.4
Hopi Acala 50	3.3	8.1	1.39	8.2	2.02	7.7
Acala 1517	2.9	10.4	1.23	9.1	1.71	8.9
Deltapine 14	2.8	10.3	1.21	9.3	1.64	9.1
Coker 100 Wilt	2.7	9.3	1.02	8.9	1.60	8.4
Stoneville 2B	2.7	7.7	1.05	8.3	1.61	7.3
Rowden 41B	2.6	10.0	1.17	9.5	1.51	7.7
Rayon (viscose)	2.95	12.5	2.34	13.4	2.50	10.0

tension must be accurately measured or estimated. While the spacing between jaws is often specified as the gage length, the true gage length of a bundle is the sum of this spacing width and the "effective slip length" of fibers within the jaws. The effective slip length is here defined as the length which, when added to the spacer width, would give the observed elongations if the bundle were free to elongate to a point where it would be positively gripped.

From mechanical theory it can be shown that effective slip length is proportional to the breaking load and inversely proportional to the force normal to the bundle and the coefficient of friction between the fiber bundle and the jaw. If a bundle is several fiber diameters thick, bundle thickness might also affect slip length, especially if the coefficient of friction of fiber on fiber differs from that of fiber on the jaw. However, this was neglected as of secondary importance at longer gage lengths. When gage length is increased, both tenacity and strain at break are reduced because of the increased probability of inclusion of weaker "weakest points" [11, 19]. For a fiber such as cotton having an essentially linear average stress-strain curve the reduction in tenacity is proportional to reduction in strain at break [5, 10]; therefore, the ratio of breaking stress to breaking strain (modulus) is essentially constant. If the slip length is constant at two gage lengths when the breaking load of the bundle and the normal jaw pressure are constant, the equation

$$\text{Modulus} = T_1G_1/e_1 = T_2G_2/e_2 \qquad (1)$$

should hold; subscripts 1 and 2 refer to the two gage lengths; T is tenacity; G is gage length; and e is actual elongation at break. Since the gage length is equal to the spacer width plus the slip length, the latter, in first approximation being the same in both instances,

$$\frac{T_1(S_1 + P)}{e_1} = \frac{T_2(S_2 + P)}{e_2} \qquad (2)$$

where P is the slip length and S_1 and S_2 are the spacer thicknesses. If S_1 is zero then

$$P = T_2S_2e_1/(T_1e_2 - T_2e_1) \qquad (3)$$

Equation (3) was used to estimate the slip length at each spacer width S_2. By this method, when the breaking load is 5 kg, the slip length of untreated cotton bundles in Pressley [2] jaws tightened with a torque of 8 lb-in. on the screw is estimated to be about 0.5 mm. When a 5-mm spacer is used, the error of estimation may be as high as 0.2 mm; however, this results in an error of less than 4% in true gage length. Since an extensive study to measure "slip length" is in progress the experimental proof of the validity of equation (3) will not be given at this time. However, preliminary results indicate that it is valid. It was desired to have bundle measurements at a gage length comparable to that used in the single-fiber tests, i.e., 7 mm. However, measurements with a 7-mm spacer in the jaws were found to be impractical since a greater proportion of the short but useful fibers must be combed out in eliminating all fibers shorter than the combined thickness of the jaws and spacers. Therefore, the strengths of fiber bundles measured with spacers of 2.5 and 5 mm were computed to 7-mm gage length by extrapolation from a plot of logarithm of gage length vs.

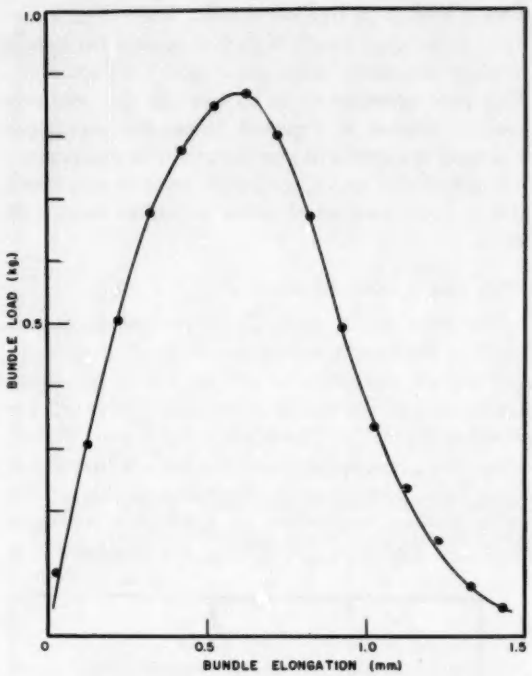

Fig. 3. Load-elongation curve for a bundle of fibers calculated from breaking loads and elongations at break of 300 single fibers of the Coker 100 Wilt variety.

strength, according to the relation developed by Peirce [11].

Results and Discussion

Load-Elongation Curve

In Table I are given mean single-fiber and flat-bundle tenacities and elongations at break for the seven cottons and the continuous-filament rayon measured at or computed to 7-mm gage length. Given also are the calculated maximum bundle tenacities and corresponding elongations at break at 7-mm gage length, determined from the single-fiber measurements. In a bundle of fibers stressed nearly to rupture, those fibers with elongations at break less than the elongation of the bundle at maximum bundle load do not contribute to bundle strength. Also, the fibers possessing an elongation greater than the elongation at the maximum bundle load are not fully loaded and do not contribute their full strength to the bundle strength. An ingenious method of calculating maximum possible bundle efficiency has been developed by Platt et al [13, 14]. This method utilizes the slope of the stress-strain curve (modulus) near break and the coefficient of variation of elongation at break of the fibers. This derived formula assumes an essentially normal distribution of elongations at break.

Since the frequency distribution of breaking elongations of single cotton fibers is somewhat skewed, a more direct method has been applied in the present study by classifying the single fiber data into elongation-at-break groups. As the average stress-strain curve of cotton is nearly linear, the load per unit of elongation of a group of fibers is B_a/E_a where B_a is the total breaking load of fibers in the group, and E_a is the median elongation at break of the fibers of the group.

As all fibers of elongation less than E_a will have broken when this elongation is reached, the load per unit of elongation on the bundle will be the sum of B/E for all groups of elongation at break equal to or greater than E_a. Then

$$L_a/E_a = \sum_{a}^{m} B/E \qquad (4)$$

where L_a is the load on the bundle at elongation E_a and m is the group of maximum elongation. The bundle load, L_a, then becomes

$$L_a = E_a \sum_{a}^{m} B/E \qquad (5)$$

In practice, the single-fiber data are classified into elongation-at-break groups and values of B/E are calculated from the total breaking load and average elongation for each group. The bundle load, L, obtained from equation (5) reaches a maximum value which is the calculated maximum breaking load. It then decreases due to fiber breakage. A load-elongation curve of a bundle calculated thus from the single-fiber data is shown in Figure 3. The shape of this curve is in agreement with that of both published bundle force-extension curves [17] and bundle curves obtained in this study. From the maximum load, total number of fibers, and average linear density of the fibers the maximum bundle tenacity for each sample of cotton was calculated. Elongation at calculated maximum bundle tenacity was taken as the elongation at maximum load.

Calculated maximum bundle tenacity of the rayon was derived directly by tabulating the load on each

fiber at each elongation interval. The sum of the loads at any elongation gives the calculated maximum bundle load at that elongation. Since the variance of breaking load and elongation at break were less for rayon than for cotton, only 50 rayon fibers were used to get a value comparable in accuracy to that from 300 cotton fibers.

Fiber and Bundle Tenacity

In Figure 4 is shown the relation of mean single-fiber tenacity to flat-bundle tenacity (curve *A*) and the relation of maximum bundle tenacity (curve *B*) calculated from the single-fiber data to the flat-bundle tenacity. The relation in each case appears to be good. It is seen, however, from curve *A* that the single-fiber tenacities are more than double the corresponding measured flat-bundle tenacities. The large departure of the mean single-fiber tenacities from perfect correspondence with the measured flat-bundle tenacities may be accounted for, in part, by variance in elongation at break of the fibers and by the shape of the stress-strain curve of the fibers. The average ratio of calculated maximum bundle tenacity to measured flat-bundle tenacity is 1.50, that of mean single-fiber tenacity, 2.27.

The discrepancy between the maximum bundle tenacity calculated from single-fiber tests and the flat-bundle tenacity can also be looked upon as a 67% efficiency for the flat-bundle test in obtaining the maximum strength from the fibers. The loss of 33% in efficiency may be caused largely by the low and nonuniform initial tension in the fibers of the bundle, by nonuniformity in slip length of individual fibers in the bundle, by shearing forces on the fibers at the edge of the steel jaws, and by nonparallelism of fibers in the bundle. Recent tests have shown that an increase in tension on the bundle to about 0.1 g per fiber before closing the jaws increases the tenacity. This increase is apparently due to more uniform initial tension on the fibers of the bundle.

It is known that the relation of fiber strength to gage length varies with cottons; that is, certain varieties tend to have fibers with more weak points per unit length than do others, and, therefore, strength drops off more than others with a given increase in gage length [2]. It is therefore to be expected that in a series of cottons a poor correlation might exist between different measurements of fiber strength or elongation when not made at the same gage length. This is seen to be true when mean single-fiber tenacity at 7-mm gage length is plotted against flat-bundle tenacity measured with zero spacer (Figure 5). This poor correlation, in contrast to the relatively good correlation in Figure 4, shows the importance of testing at equivalent gage lengths when comparing strength of cottons. Gage length must be considered also in stress analysis of yarns, as will be mentioned later.

Fiber and Bundle Elongation

The relations of mean single-fiber elongation at break to flat-bundle elongation at break (curve *A*) and also of elongation at the calculated maximum bundle load to flat-bundle elongation (curve *B*) are shown in Figure 6. The relationship is good in each comparison, and the slopes of the lines of best fit are about 2.0. This is about the same as that of the curve relating single-fiber to flat-bundle tenacities shown in Figure 4. However, the elongations of

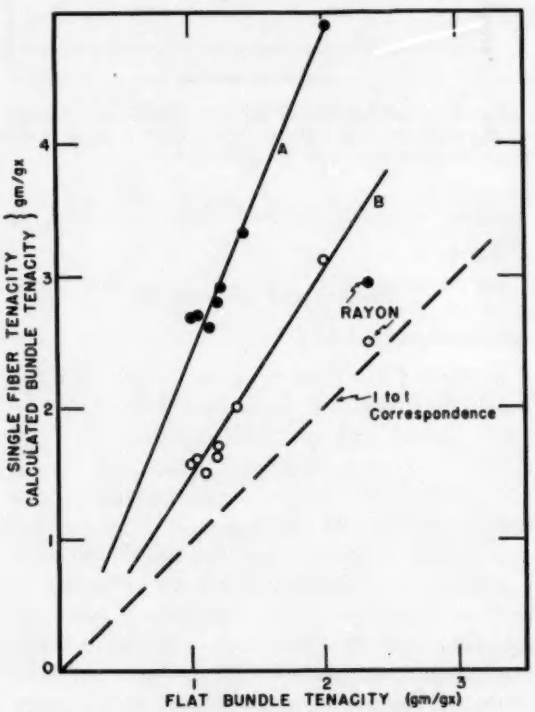

Fig. 4. Relation of single-fiber tenacity to flat-bundle tenacity (curve *A*) of and calculated bundle tenacity to measured flat-bundle tenacity (curve *B*) for seven cottons and one rayon. All measurements were made at or computed to 7-mm gage length.

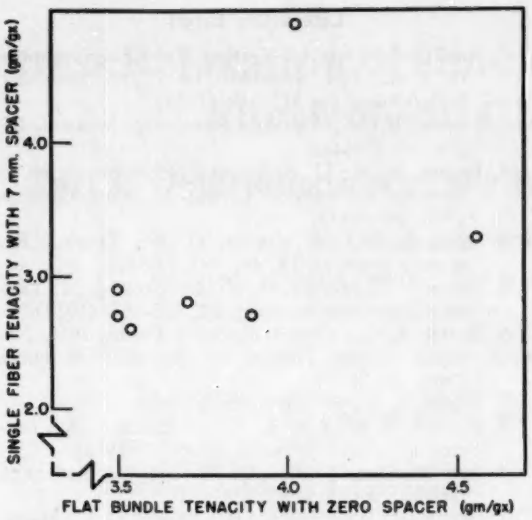

Fig. 5. Single-fiber tenacity at 7-mm gage length plotted against flat-bundle tenacity with zero jaw spacer for seven varieties of cotton.

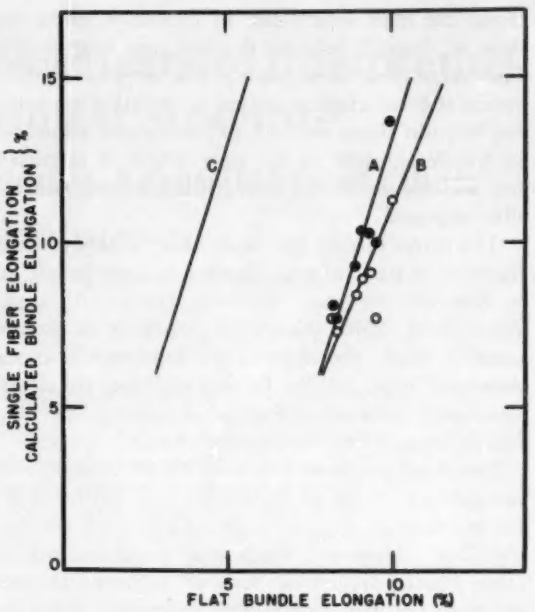

Fig. 6. Relations of single-fiber elongation at break to flat-bundle elongation at break (curve *A*) and of elongation at calculated maximum bundle load to flat-bundle elongation at break (curve *B*) from fiber measurements made at or computed to a gage length of 7 mm. Curve *C* represents the relation of single-fiber elongation to flat-bundle elongation when reduced by 5%.

the flat bundles are about as large as those of the single fibers in contrast to the ratio for tenacities, where the values are about 1 to 2. This difference can be attributed to variation in initial tension on fibers when tests are made by the two methods. Flat-bundle tests show a low modulus at low load, which can be ascribed to kinkiness of the fibers. The calculated load-elongation curve (Figure 3) does not show this low initial modulus because kinks were removed in the single-fiber tests by the initial load of 0.2 g per fiber. Application of higher tensions to the bundles before closing the jaws has caused lower elongation-at-break values. If we assume that a part of the actual bundle elongation is caused by the kinkiness which is readily observed by increasing the initial load from 0.01 to 0.2 g on single fibers, we can subtract 5% elongation of the total of about 9.5–10% from the actual bundle elongation and obtain the relation shown by curve *C* in Figure 6. The relation shown by curve *C* is then consistent with that of the relation of mean single-fiber tenacity to flat-bundle tenacity shown in Figure 4.

Significance of Results

The flat-bundle test, in addition to providing results equal in many respects to those from single-fiber tests, requires much less time and offers other advantages. In both yarn and fabric constructions fibers are used in groups. It can be shown [13] that the factors affecting bundle strength affect yarn and fabric strength similarly although many geometrical factors which affect yarn strength do not affect bundle strength. Although these geometrical factors are not included in bundle tests, an improved correlation between bundle strength and yarn or fabric strength can be obtained by testing at a gage length approximately equal to the effective grip length between fibers in the yarn or fabric construction. The actual or effective grip length of fibers in the yarn is variable and thereby difficult to deal with in yarn mechanics. The correlation of yarn strength with fiber-bundle strength of many cotton samples measured at various gage lengths [2, 6, 12] has given an indication of the effective grip length.

When flat-bundle tests are made at two gage lengths, that part of the variance in either fiber tenacity or elongation at break caused by weak points

along the fiber length can be estimated, since the drop in strength between the two gage lengths is a function of these weak points. The variation in elongation at break of fibers caused by variation in modulus between fibers will not in itself cause reduction in bundle strength as the gage length is increased but will reduce bundle strength below mean single-fiber strength.

The rayon used in this study showed only a small decrease in tenacity with increase in gage length, as is observed for most synthetic fibers. Although rayon fibers exhibit considerable variation in elongation at break, the slope of the stress-strain curve decreases near bundle break, resulting in closer agreement between calculated maximum possible bundle tenacity and flat-bundle tenacity.

For many purposes, values of bundle tenacity and elongation at break as determined with the Stelometer are comparable in usefulness to those of the single fiber. However, single-fiber measurements of other elastic properties, such as recovery characteristics, are not represented accurately with the present bundle technique due to design of the instrument and slippage of fibers in the jaws.

Conclusions

Good correlation is found between single-fiber and flat-bundle strength and between single-fiber and flat-bundle elongation-at-break values when measurements are referred to equivalent lengths of specimen. The difference in strength and elongation values of flat bundles and those calculated from mean single-fiber values can be reasonably ascribed to bundle mechanics and differences in the test methods and in sampling errors.

Flat-bundle tenacity and elongation-at-break values are comparable in accuracy to those of single fibers and should be valuable for predicting yarn and fabric behavior. However, single-fiber tests are still essential in providing information on many other elastic characteristics.

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Stress Relaxation of Fibers as a Means of Interpreting Physical and Chemical Structure[1]

Part I: Determination of the Relative Accessibility of Fibers

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Abstract

A summary of some preliminary studies on the stress-relaxation behavior of synthetic and cellulosic textile fibers in distilled water and hydrochloric acid is reported in this paper. The results are interpreted in terms of the molecular and physical structures of these materials. Identical stress-relaxation behavior of many diverse materials in distilled water indicates that the relaxation is caused by scission of the weaker secondary linkages. It is concluded that the drastic reduction in stress following addition of hydrochloric acid is caused by the rupture of primary bonds. Widely differing relaxation behavior of a series of synthetic fiber samples having different draw ratios is directly attributable to the degree of order of these fibers.

Stress-relaxation measurements on the cellulosic fibers in hydrochloric acid are interpreted in terms of relative accessibility. The data presented show that the relative accessibility is a function of the concentration of the acid reagent and the temperature at which measurements are made. Relative accessibility data reported in the literature are compared with values obtained from stress-relaxation measurements for a number of cellulose samples. All the samples indicate the same general ranking as a function of fiber type, but the results vary widely in reported values.

Introduction

Chemical investigations of the molecular structures in textile fibers consider only the strong intramolecular forces (those within a molecule). These primary valence bonds hold the atoms together within a molecule, thereby being responsible for its stability. Examples of such bonds are the carbon-carbon bond in polyethylene, the carbon-nitrogen bond in nylon, and the carbon-oxygen bond in Dacron.[4]

Most investigators usually ignore the weaker intermolecular forces (those between molecules). These secondary valence forces cause molecules to exert forces on each other and contribute to the fiber-forming properties of linear polymers. Examples of such bonds are hydrogen bonds and van der Waals forces in rayon, cotton, and ramie; van der Waals forces in polyethylene; and hydrogen bonds and van der Waals forces in nylon.

Studies of physical structure consider the ordered arrangement and regular occurrence of atomic or molecular units in space. Until recent years, such investigations were possible only through the use of X-ray analysis. In studying the physical properties of fibers, materials are encountered running the entire range from the highly crystalline to the almost completely amorphous state. Amorphous polymers include vinyl polymers, such as polyvinyl acetate, polyalkyl methacrylate, and polystyrene, which apparently do not crystallize under any conditions. Others, such as polyvinyl chloride and polyisobutyl-

[1] This article is based upon part of a thesis submitted by T. Lemiszka in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

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[4] Du Pont polyester fiber.

ene, can be made to crystallize by stretching. However, none of the so-called crystalline polymers, such as polyethylene, nylon, and Dacron, are believed to achieve 100% crystallinity.

Solvents and chemical reagents are capable of modifying or destroying bonds within and/or between the molecules of a fiber. The attack may be made selective for either bond type by the proper choice of attacking reagent. The action of reagents, however, is also governed by the physical structure. Heuser [23], for example, in a recent review, has pointed out that cellulose reactions are governed by the physical structure of cellulose as well as by its chemical nature.

According to present-day concepts [16, 31, 36, 37], cellulose consists of long macromolecular chains forming a distribution of ordered regions ranging from the completely amorphous to the completely crystalline states. There is no sharp line of demarcation between the amorphous and the crystalline regions. The less well-ordered regions may range from completely amorphous to imperfectly crystalline material. Individual chains may pass through a crystalline region, an adjacent amorphous region, another crystalline region, and so on. It is well known that the ratio of ordered to disordered material has an important influence on the physical and chemical properties of a fiber. However, the degree of crystallinity as such is not as important as the amount of reactive material in the cellulose. This is ordinarily defined as accessibility and in essence is an experimental determination denoting the fraction of total material available or accessible to any reagent under given experimental conditions.

This paper is concerned with the determination of the relative amount of accessible material present in fibers by employing the technique of stress relaxation of fibers immersed in an attacking reagent. It presents in some detail data on undrawn and drawn nylon, Dynel, Dacron, and other synthetic fibers. Data on textile rayon, ramie, and other cellulosic fibers will also be presented. The effect of such variables as the concentration and temperature of reagent upon the determination of relative accessibility is included. Relative accessibilities of a number of cellulose samples determined from stress-relaxation measurements are presented and compared with accessibilities reported in the literature.

Theory

Various aspects regarding the definition, history, and discussion of viscoelastic behavior and stress relaxation have been presented by Leaderman [28], Alfrey [1], Zener [50], Treloar [48], Mark and Tobolsky [31], and Wakeham [49]. There has been a limited amount of work reported on cellulosic fibers. Smith and Eisenschitz [44] studied the stress relaxation of rayon, cellulose acetate, and silk and unsuccessfully attempted to interpret their results in terms of the Boltzman "after-effect" theory. The final retractive force supported by cellulose filaments was studied by Hermans [14]. Andersen and co-workers [2, 3, 4, 5, 6] investigated the mechanical properties of cotton and rayon fibers. A new method for evaluating stress-relaxation experiments on cotton and rayon cords was described by Burleigh and Wakeham [9]. Eyring and co-workers [26, 27, 35] studied the mechanical properties of cotton fibers using stress relaxation in air, water, acids, and alkalis.

Many methods have been proposed to estimate the amounts of disordered (noncrystalline or accessible) material in cellulose. These methods may be placed in two categories: physical methods and chemical methods.

Physical Methods

Physical methods include the following: X-ray diffraction [16, 19, 20, 21, 22], moisture regain [15, 24], nonfreezing water [30], density [15, 16, 17, 18], and deuterium oxide exchange [11].

Chemical Methods

Chemical methods may be classified into two groups: (1) those reactions in which the hydrogen of the hydroxyl group is replaced and (2) those reactions in which a reagent brings about a scission of the primary linkage. The former is generally measured by the ratio of converted to unconverted hydroxyl groups, and the latter is generally measured by following the course of the reaction kinetically.

Reagents which have been used in the hydroxyl-group conversion method include thallous ethylate dissolved in various ethers plus methyl iodide [7], diazomethane dissolved in ether [40], sodium in liquid ammonia [47], radioactive sodium hydroxide [41], iodine [43], allyl materials [47], and formic acid [34, 45, 46].

Reagents which have been used in the degradative chemical method include periodic acid and periodates [13, 47], chromium trioxide in acetic acid-acetic anhydride mixture [12], hydrochloric acid and ferric

chloride [10, 33], and hydrochloric acid and other inorganic acids [8, 29, 39]. Organic and inorganic acids have also been used to study the mechanism of acid hydrolysis [31], the "limiting" D.P. of crystalline units [32], and the proposed existence of acid-sensitive weak links [38, 42].

Experimental Procedure

Apparatus

Apparatus for the stress-relaxation experiments with which this work was concerned was designed and constructed in these laboratories by Kubu [25]. It essentially consists of six linear variable differential transformer ring dynamometer assemblies with their associated electrical systems, water-jacketed tubes, mechanical supports, and rhodium-plated clamps. A Brown Multipoint Recording Potentiometer recorded the stress relaxation as a function of time.

Technique

A single filament was mounted between clamps and immersed in distilled water for approximately 24 hr to permit the fiber to be thoroughly wetted. Following the soaking period, the fiber was extended to a predetermined force, usually around 5 g, and the stress was allowed to relax for about 24 hr in distilled water. At the end of this time, the distilled water was siphoned off and replaced with hydrochloric acid previously adjusted to the temperature of the experiment. The subsequent stress relaxation was then observed for another 24 hr. Preliminary work showed the synthetic and regenerated cellulose fibers to be sufficiently uniform and homogeneous to enable the use of single filaments in most instances for each acid concentration and temperature.

Method of Calculation

On the assumption that cellulose contains material at varying degrees of order, the rates of scission of bonds should vary continuously from very rapid in the amorphous regions to very slow in the crystalline regions. Hence, if the logarithm of the stress supported by the fiber is plotted against time, a curve should result which approaches linearity when all the acessible stress-supporting bonds have been ruptured. If this portion of the curve is extrapolated to the ordinate, a value is obtained which is a function of the fraction of bonds at zero time in the non-accessible material. The fraction of bonds which is accessible is the complement of the fraction inaccessible. This technique of measuring accessibility by extrapolating the linear portion of the reaction curve to the ordinate was proposed by Nickerson [33] and later employed by Mark et al. [11], Timell [47], Glegg [12], Philipp, Nelson, and Ziifle [39], Lovell and Goldschmid [29], and many other workers using a variety of physical and chemical methods.

Results and Discussion

Synthetic Fibers

Stress-relaxation curves for three nylon samples immersed successively in distilled water and 1.0 *N* hydrochloric acid at 30°C are shown in Figure 1. The fibers are undrawn nylon and two drawn nylons, the latter having draw ratios of 2.02 and 5.99. X-ray patterns for these samples indicate the existence of a progressive increase in order with increasing draw ratio. In the figure, arrows indicate the point of addition of the reagent. Because of the difficulty of measuring the force at zero time, the value of force at 60 min is arbitrarily taken as a reference and all other forces are divided by it. These normalized forces are plotted linearly against the logarithm of time, this form of plot being convenient to represent data over such long time intervals.

It is seen that fibers of the same material but differing in their degrees of order relax differently in distilled water and hydrochloric acid. In water, the normalized force relaxes rapidly for the undrawn nylon, less rapidly for the nylon of draw ratio 2.02, and least rapidly for the nylon of draw ratio 5.99. Furthermore, the final normalized force supported by the fiber (following relaxation in distilled water and prior to addition of acid) also increases as the degree of order in the fiber increases.

Following the addition of acid, there occurs a drastic reduction in stress which is more pronounced than that obtained in water alone. This effect is shown in Figure 1 and is more strikingly apparent in Figure 2, which presents only the portions of the stress-relaxation data for the same fibers after the addition of 1.0 *N* hydrochloric acid. Since extrapolation of the linear portion of the curve to zero time should give the fraction of all the original bonds which are inaccessible to the reagent, the fraction of bonds present in the accessible regions is obtained

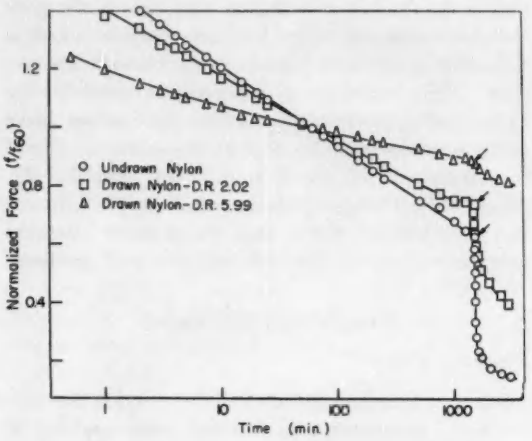

Fig. 1. Stress-relaxation data for undrawn and drawn nylons, first in distilled water and then (after arrows) in 1.0 *N* hydrochloric acid.

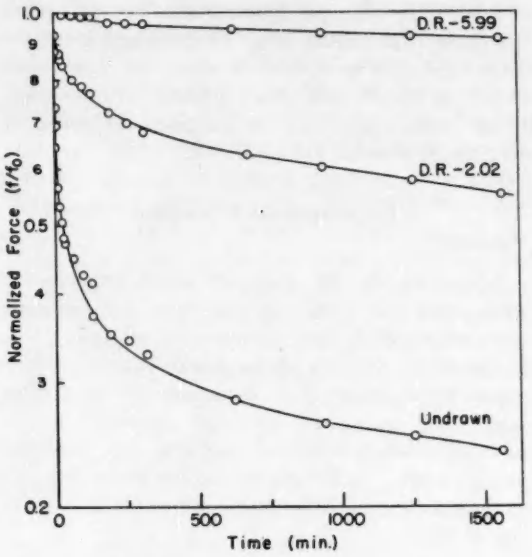

Fig. 2. A replot of Figure 1 for those portions of the stress-relaxation curves following the addition of 1.0 *N* hydrochloric acid.

by difference from unity. Figure 3 presents relative accessibility values determined in this manner plotted against the draw ratios of the nylon samples. The reduction in relative accessibility due to increased orientation resulting from increased draw ratio is thus very marked. Apparently the decrease in relative accessibility is nearly a "first-order process" with respect to draw ratio.

Figures 4 and 5 present stress-relaxation curves for two Dynel and two Dacron samples, respectively, immersed successively in distilled water and 1.0 *N* hydrochloric acid at 30°C. The fibers are an undrawn Dynel and a drawn Dynel, the latter having a draw ratio of 8.25, and two drawn Dacrons having draw ratios of 3.99 and 5.99. Although X-ray patterns of these samples are not available, it is logical to believe that there is a progressive increase in order with increasing draw ratio. Since these materials do not react with hydrochloric acid in the same manner as does nylon, their accessibilities were not determined.

Figures 1, 4, and 5 indicate that fibers of the same material but differing in the degree of order relax differently in distilled water and hydrochloric acid. Inasmuch as all the experimental conditions were identical, it is obvious that the variations in stress-relaxation behavior must be caused only by differences in the physical structures of these fibers. These differences cannot be due to the types of primary and secondary linkages, therefore, but must be related to the availability of such linkages to the action of solvents and reagents. This concept is commonly known as accessibility. It has been broadly defined as the extent of the total material present which is accessible to a certain reagent under the stated experimental conditions, such as concentration, time, and temperature.

Although the exact relationship between accessibility and the noncrystalline portions of a fiber is still in dispute, it is generally agreed that there is a direct relationship; i.e., as the degree of disorder increases, accessibility increases. The experimental phenomena observed here are thus readily interpretable in terms of accessibility. It is well known that the degree of order increases as the draw ratio becomes greater. Hence the number of bonds, both primary and secondary, susceptible to attack in the disordered regions must decrease. It is generally agreed that bonds in the crystalline regions are protected against rapid chemical attack until made available by diffusional action, which is a very slow process. Those fibers with greater accessibility will suffer more extensive attack. Stress-relaxation behavior should therefore be capable of being used to determine the relative accessibilities of fibers differing in degree of order.

Figure 6 presents points from stress-relaxation curves of commercially drawn samples of polyethyl-

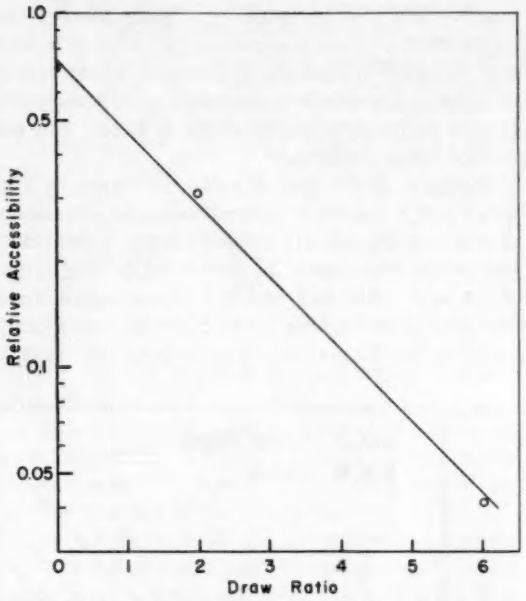

Fig. 3. Relative accessibility values for nylon fibers of different draw ratios plotted semilogarithmically against draw ratio.

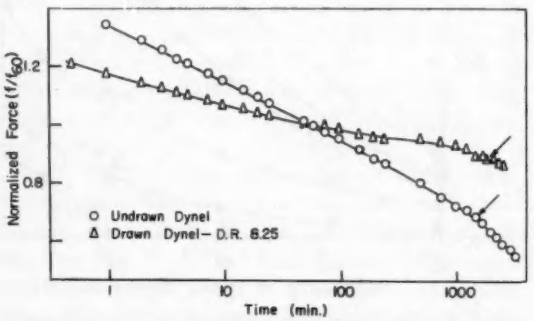

Fig. 4. Stress-relaxation data for undrawn and drawn Dynels, first in distilled water and then (after arrows) in 1.0 *N* hydrochloric acid (f/f_{60}—force normalized to changes at 60 min).

ene, Teflon, Orlon,[5] Dynel, nylon, Dacron, and textile rayon immersed in distilled water at 30°C. The solid line through the points on this figure is that of Kubu [25] for wool, silk, and nylon. These materials contain many different types of primary and secondary linkages. Since the secondary linkages are known to have bond strengths of approximately 5 kcal/mole or less, whereas the primary linkages

[5] Du Pont acrylic fiber.

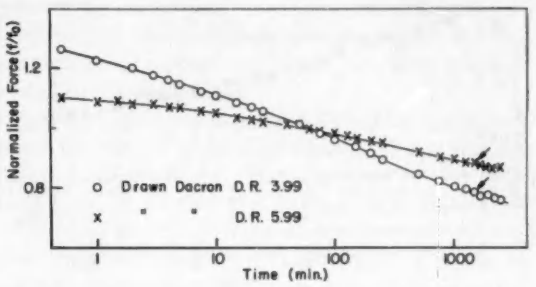

Fig. 5. Stress-relaxation data for drawn Dacrons, first in distilled water and then (after arrows) in 1.0 *N* hydrochloric acid (f/f_0—force normalized to changes at time of acid addition).

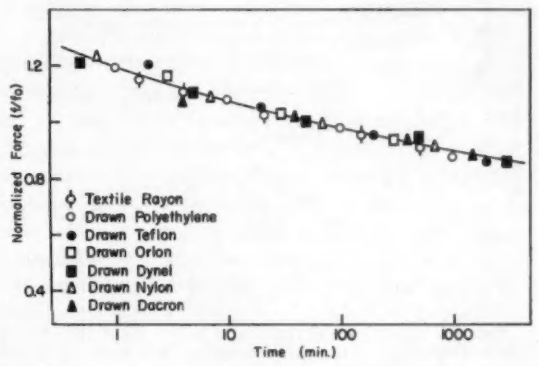

Fig. 6. Stress-relaxation data for a variety of synthetic fibers in distilled water.

have bond strengths as high as 150 kcal/mole, it seems highly probable that stress relaxation in distilled water is brought about by the scission of the much weaker secondary bonds. Because these secondary bond strengths are so small they cannot be differentiated by this technique. Therefore, assuming that the stress-relaxation process in water is governed by secondary bond scission, it is reasonable for the stress relaxations of all these materials to be in agreement. It is also of interest to observe that the stress-relaxation behavior of textile fibers immersed in water is similar to that observed for vulcanized rubber, wool, and other cross-linked substances but different from that observed for noncross-linked rubbers such as polyisobutylene. Both textile fibers and cross-linked rubbers possess three-dimensional structures; in the former substances there are strong covalent longitudinal linkages and weak secondary lateral linkages, whereas in the latter

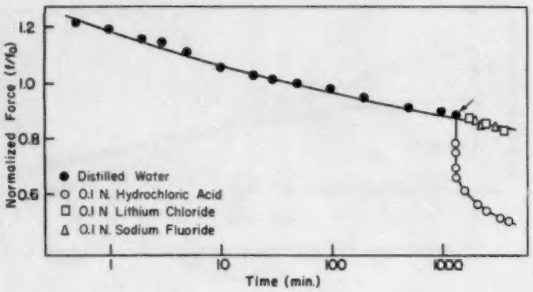

Fig. 7. Stress-relaxation data for textile rayon, first in distilled water and then (after arrow) in various primary and secondary valence bond-breaking reagents, all at 30°C.

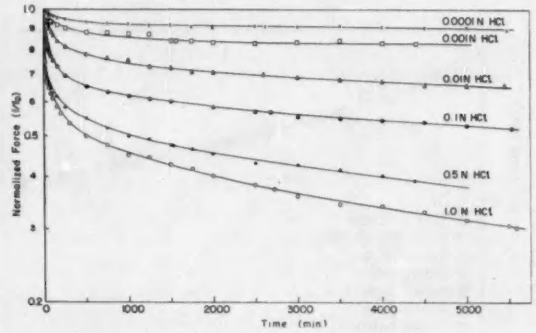

Fig. 8. Typical stress-relaxation curves for textile rayon for those portions of the data following the addition of different concentrations of hydrochloric acid.

substances both longitudinal and lateral linkages include strong covalent bonds. Noncross-linked rubbers, on the other hand, have extremely weak secondary linkages which are brought into play only when they are in a highly extended state.

Regenerated Cellulosic Fibers

Figure 7 presents stress-relaxation curves of filaments of a textile rayon immersed in distilled water followed by immersion of the different filaments in 0.1 *N* solutions of lithium chloride, sodium fluoride, and hydrochloric acid at 30°C. It is seen that neither of the salt solutions causes a reduction in stress from that occurring in distilled water alone. Hydrochloric acid, on the other hand, does show a marked effect. It is known that lithium and fluoride salts are powerful agents for rupture of hydrogen bonds, which, together with van der Waals forces, make up the secondary bond structure of cellulose. Indeed, strong aqueous solutions of these salts will dissolve silk and polypeptides. Since there is no major effect of these reagents on the cellulose beyond that expected to continue in water. it would appear that the acid is attacking primary bonds, presumably the 1,4-β-glucosidic bonds of the cellulose, and not the secondary linkages.

Similarly, in the case of nylon, as shown in Figures 1 and 2, the 1.0 *N* hydrochloric acid presumably is attacking the primary amide linkages, a reasonable supposition based upon the known solubilizing action of the acid. The lack of effect of acid upon Dynel and Dacron in Figures 4 and 5, on the other hand, supports the known fact that hydrochloric acid is

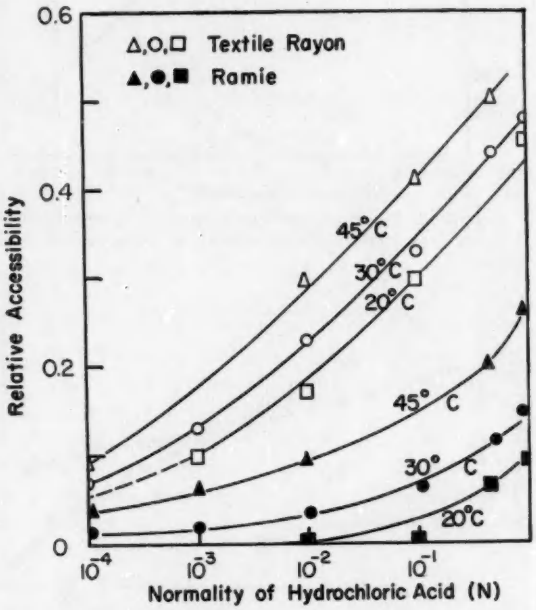

Fig. 9. The effect of concentration and temperature of hydrochloric acid on the determination of the relative accessibility of textile rayon and ramie.

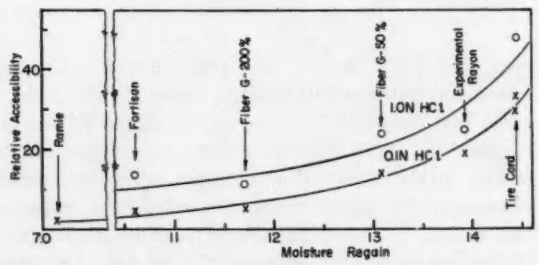

Fig. 10. Relative accessibility data for different cellulose samples shown as a function of their moisture regains.

TABLE I. Moisture Regain and Stress-Relaxation Accessibilities of Cellulose Fibers

Sample	Moisture Regain 70°F, 65% R.H. (%)	Accessibility at 30°C Measured by Stress Relaxation in 0.1 *N* HCl	Accessibility at 30°C Measured by Stress Relaxation in 1.0 *N* HCl
Ramie	7.3	4	—
Fiber G—200%	11.7	5	11
Fortisan	10.6	5	14
Fiber G—50%	13.1	14	24
Experimental Rayon	13.9	19	25
Tire Cord	14.4	29	—
Textile Rayon	14.5	33	48

not the reagent to which the primary linkages in these substances are susceptible.

Figure 8 presents those portions of the stress-relaxation data for different individual textile rayon filaments after addition of six concentrations of hydrochloric acid, namely, 0.0001 *N*, 0.001 *N*, 0.01 *N*, 0.1 *N*, 0.5 *N*, and 1.0 *N*, all at 30°C. Another normalized force—the force at any moment divided by the force immediately preceding acid addition—is plotted logarithmically against the time in minutes, where the time of acid addition is set as zero time. None of the curves indicates a first-order reaction; all six curves show a progressive change in the rate of reaction as observed for practically all heterogeneous cellulose reactions, i.e., a rapid rate in the initial stages followed by slower rates in the later stages, with a final nearly constant rate after a long time of operation.

Using the technique previously described, the relative accessibilities of textile rayon were obtained from these curves at all six concentrations and at tempatures of 20, 30, and 45°C. These results, presented in Figure 9, show the effect of acid concentration and temperature upon the determination of the relative accessibility of textile rayon. Similar results for the effect of these variables upon the determination of relative accessibility of ramie are presented in the same figure.

The accessible fractions in both textile rayon and ramie increase as either acid concentration or reagent temperature increases. Many workers in this field have pointed out that the determination of accessibility is an exact experimental quantity only for the conditions under which it is determined. Some of the important variables are temperature, concentration, size and polarity of the reagent molecule, degree of swelling, and morphology of the fiber. The results in Figure 9 for textile rayon and ramie support the view that in reporting accessibilities the experimental conditions must be stated in detail.

Figure 10 and Table I present relative accessibilities determined from stress-relaxation measurements of a number of cellulosic materials in both 0.1 *N* and 1.0 *N* hydrochloric acid compared with their moisture regains at 70°F and 65% relative humidity. The moisture-regain behavior is included since it has often been employed to determine sorption ratios, which are concluded to be proportional to accessibility. It is seen in Table I that both methods list the cellulose samples in the same order, although the relation between accessibilities determined by the two methods is not linear. The rankings also agree with those reported by other investigators, who used many different methods to determine accessibility. The relative accessibilities obtained with 1.0 *N* acid are all higher than those obtained with 0.1 *N* acid, again substantiating the belief that in reporting accessibility data the experimental conditions used in their determination must be reported in detail.

Table II presents a summary of reported accessi-

TABLE II. Survey of Accessibility* Measurements by Other Investigators

Method	Ramie	Cotton	Mercer. Cotton	Wood Pulp	Mercer. Wood Pulp	Fiber G	Fortisan	Cordura	High-Tenacity Rayon	Viscose Rayon
X-ray diffraction [22]	29	31	—	35	52	47	51	—	60	60
Moisture regain [24]	—	44	—	53	69	72	63	—	87	79
Density [15, 16]	40	40	—	50	—	—	—	—	—	75
Calorimetry [30]	—	13, 17	23	—	—	—	—	48	—	—
Deuterium exchange [11]	—	44	—	55	74	67	—	—	86	68
Thallous ethylate [7]	0.25	0.4	24	—	—	—	—	—	77	—
Formic acid [34]	—	28†	—	47	—	65	—	—	—	54
Formic acid [45, 46]	—	16‡	28	—	—	—	—	—	—	21–27
Hydrolysis oxidation [10, 33]	—	5–9	11–16	8–10	—	—	—	38	—	32
Acid hydrolysis [8, 29, 39]	5	12	12–18	—	—	19	17	—	—	—

* Accessibility, disordered material, or noncrystalline material.
† 98% formic acid, 55°C, 15 hr.
‡ 90% formic acid, 30°C, 12 hr.

bilities for different cellulose samples obtained from a variety of experimental techniques by independent investigators. There are three generalizations which can be drawn from these data. The first is that nearly all the methods, including the technique described in this paper, rank the cellulose samples in the same order. The second generalization to be drawn is that the physical methods generally give higher values than do the chemical methods. The results in Table I agree reasonably well with the magnitudes of the accessibilities reported for other chemical methods. This agreement with the other chemical methods offers further reason to believe that the stress relaxation of cellulosic filaments following acid addition is caused by the scission of primary linkages. The third generalization is that the values reported by any method are dependent upon that method and the experimental conditions and cannot have absolute significance.

Summary and Conclusions

1. A new technique for determining the relative accessibility of textile fibers is presented. It employs the measurement of the stress relaxation of the fiber in an attacking reagent following stress relaxation in distilled water.

2. For a set of undrawn and drawn nylon samples, the rate of stress relaxation of nylon immersed in distilled water decreases as its draw ratio, and hence degree of order, increase. Furthermore, the normalized stress supported by the fiber at the end of stress relaxation in distilled water and prior to the addition of acid is higher for a fiber possessing a higher draw ratio.

3. Following stress relaxation in distilled water, the addition of 1.0 *N* hydrochloric acid to the same series of nylon fibers brings about a drastic reduction in stress, with the magnitude of the stress reduction being inversely proportional to the degree of order of the fiber.

4. The addition of 1.0 *N* hydrochloric acid to a series of relaxing Dynel and Dacron fibers, also differing in draw ratio and following stress relaxation in water, causes no reduction in stress from that occurring in water alone. This lack of effect merely confirms the fact that this reagent is not capable of producing primary bond rupture in these materials.

5. Normally oriented samples of wool, silk, rayon, polyethylene, Teflon, Orlon, Dynel, nylon, and Dacron exhibit identical stress-relaxation behavior in distilled water at 30°C within experimental error. It is therefore postulated that stress relaxation in water is caused by the scission of any of the weaker secondary linkages present in these materials.

6. The members of the nylon, Dynel, and Dacron series, varying in the degree of order only, exhibit widely differing stress-relaxation behavior in distilled water at 30°C. Furthermore, the reduction in stress caused by the addition of hydrochloric acid to the series of nylon fibers is more pronounced as the degree of order diminishes. These phenomena are shown to depend upon the accessibilities of the molecules in the fibers, which in turn are determined by the draw ratios.

7. The addition of hydrogen bond-breaking agents such as lithium and fluoride solutions has no effect upon the stress relaxation of rayon; hence, it is concluded that the demonstrated attack by hydrochloric acid is upon the primary bonds, generally believed to be amide and glucosidic linkages in the nylon and cellulosic fibers, respectively.

8. Relative accessibility determinations for cellulosic materials are obtained by extrapolating the linear portions of the stress-relaxation curves following hydrochloric acid addition to the zero time ordinates. The accessible fractions in both textile rayon and ramie increase as either acid concentration or temperature increases. Therefore, although accessibility is a definable quantity, its determination is relative and should be reported in a manner to indicate in detail the experimental conditions used in its determination.

9. Relative accessibility determinations for a number of cellulosic materials rank them in the same order as do measurements of moisture regain. This ranking agrees with the rankings reported by other investigators. The relative accessibilities obtained in this investigation are reasonably similar in magnitude to those reported for chemical, rather than physical, methods for determining relative accessibility.

Acknowledgment

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poration kindly supplied the textile rayon and several other cellulosic fiber samples. The work presented here was financially supported in part by the Office of Naval Research, Navy Department (Contracts No. Nonr-09000 and Nonr-09001) and in part under the general research program of the Textile Research Institute. A fellowship grant to one of the authors from Textile Research Institute made this work possible and is gratefully acknowledged.

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The Sorption of HCl by Textile Fibers[1]

II. Sorption by Modified Wool Fibers and Other Fibers[2]

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Introduction

In a previous paper which will be designated as Part I [6] the author reported the results of some experiments in which the sorption of hydrogen chloride by wool was measured under various conditions of temperature and pressure. The present paper gives the results of similar experiments carried out with modified wools and with other fibers in an attempt to throw more light on the process of sorption.

Apparatus and Methods

The apparatus and methods used were similar to those described in Part I.

Materials and Methods

The following samples were used in the experiments described: wool noils of fine quality, a 4-ply knitting yarn which had received no chemical treatment except the regular commercial scouring during manufacture, a 600-den dull nylon yarn, a 600-den bright nylon yarn, a 70-den undrawn nylon yarn, a 170-den dull Rilsan yarn, a 75-den bright Orlon[3] yarn, a 71-den bright Dacron[4] yarn, a bright Perlon staple, and silk thread (0.20 g/m) without weighting or other finishing material. In addition fibers modified according to the following methods were also tested.

Treatment of Wool with KOH

Some of the wool noils were treated with alcoholic KOH as described by Lindberg [6]. One gram of wool was immersed in a solution containing 2 g of KOH, 96 ml of 100% EtOH, and 4 ml of distilled water for 15 min at room temperature. The wool was then placed in a solution containing 1 ml conc. H_2SO_4 and 4 ml H_2O in 96 ml of 100% EtOH. After a few minutes the wool was rinsed in distilled water and dried overnight at 70°C.

Treatment of Wool with Dinitrofluorbenzene

A sample of the wool yarn was treated with 40 times its weight of a solution containing 65% $NaHCO_3$ and 50% dinitrofluorbenzene (D.N.F.B.), based on the weight of wool, for 3 hr at 60°C, after which the solution was renewed and a further treatment of 3 hr given. The solution was again renewed, and the treatment continued for another hour. The wool was then squeezed free of adhering liquid and immersed for 15 min in a large volume of $N/10$ acetic acid at 65°C. This was followed by immersion in a $N/10$ HCl solution for 1 hr at room temperature, after which the solution was renewed and the immersion continued overnight. The wool was then rinsed with distilled water and extracted with acetone for 5 hr. During the D.N.F.B. treatment, the wool was agitated continuously and in the subsequent acid treatment it was stirred occasionally. From the increase in weight (50.4%) of the dried wool it was calculated that 3.04 mM of the reagent had reacted with 1 g of wool. Another sample which had received but one 3-hr treatment with D.N.F.B. had reacted with only 0.32 mM of the reagent. For comparison in measuring the rate of sorption, a blank was prepared by treating a wool sample as for the D.N.F.B. treatment except that the D.N.F.B. reagent was omitted. This was to determine whether the heating with the sodium bicarbonate solution and the subsequent acid washing had any effect by themselves.

Treatment of Silk with D.N.F.B.

For the silk, the treatment differed somewhat from the above procedure and was based on experiments reported by Zahn and Würz [8]. Four grams of silk were treated for 7 hr at 40°C in a solution con-

[1] This paper is designated N.R.C. Report No. 3687.
[2] Part I appeared in February, 1953.
[3] DuPont acrylic fiber.
[4] DuPont polyester fiber.

taining 150 ml water, 450 ml EtOH, 7 g $NaHCO_3$, and 12 g D.N.F.B. The acid treatments that followed were similar to those given the wool sample. The increase in weight of the dried sample (11.8%) corresponded to 0.71 mM of reacting groups.

Extracted Wool

A sample of wool yarn was extracted with anhydrous ether for 2 mo in an apparatus similar to that described by Human and Speakman [4].

Oxidized Wool (α-Keratose)

A sample of wool yarn was oxidized with peracetic acid by treatment in a 4% aqueous solution of the acid at room temperature for 24 hr. After rinsing, the wool was dissolved in dilute ammonia and any insoluble matter filtered off. The clear solution was then acidified, and the precipitate separated by filtration and washed free of excess acid by rinsing with distilled water adjusted to *p*H 5.

All samples were extracted with ether and with alcohol and then equilibrated with distilled water adjusted to *p*H 5 prior to the sorption experiments.

TABLE I. HCl Sorbed (mM/g) by Intact and Modified Wool and Silk

Pressure (cm Hg)	Temperature (°C)	Intact Wool	D.N.B. Wool	Intact Silk	D.N.B. Silk
46.1	31.0	4.81	4.67*	3.58	3.12
56.5	31.0	4.98	4.88*	3.75	3.23
54.9	1.0	6.56	6.44*	4.71	4.29
After desorption (15 days)					
		1.08	1.17*	0.77	0.42
4.6	41.9	2.42	2.29		
12.8	41.9	3.07	3.14		
19.0	41.9	3.31	3.45		
51.1	41.9	4.38	4.88		
After desorption (5 days)					
		1.39	0.99		
5.3	42.0	2.52	2.47		
		2.61†			

Pressure (cm Hg)	Temperature (°C)	Intact Wool	KOH Wool	Extracted Wool	Dyed Wool	Oxidized Wool
51.9	40.7	4.31	4.35			
46.4	30.5	4.41		4.45		
52.1	40.8	4.77			3.89	
1.3	41.5	1.9‡				4.1
11.8	41.5	3.0‡				9.1
After desorption (15 days)						0.2

* First sample with 0.32 mM of reacted groups. The other figures are for the second sample with 3.04 mM reacted groups.

† Blank treated as D.N.B. wool but without the D.N.F.B. reagent.

‡ Calculated from the sorption-pressure relation obtained from the previous experiments.

TABLE II. HCl Sorbed (mM/g) by Various Fibers

Pressure (cm Hg)	Temperature (°C)	Bright Nylon	Undrawn Nylon	Bright Perlon	Bright Orlon
8.3	42.1	9.32	9.37	9.76	0.13
8.2	27.0	9.82	10.00	10.66	—
7.5	2.0	10.91	11.15	12.50	0.33
8.4*	26.5	10.00	10.00	10.66	—
8.7*	41.5	9.32	9.37	9.86	0.17
19.1	41.3	9.88	9.88	11.86	0.22
53.1	41.0	10.80	11.13	13.59	0.28
52.5	24.0	11.55	12.03	14.88	0.48
51.9	1.2	13.68	14.05	16.45	0.67
63.0*	41.6	10.90	11.12	13.95	0.39
62.5	26.0	11.72	12.03	15.01	0.55
61.6	1.5	13.90	14.34	16.69	0.77
8.3*	42.0	9.32	9.32	10.46	0.24
After desorption (11 days)					
		0.27	1.11	1.18	0.08
9.4	42.0	9.21	9.30	9.54	—

Pressure (cm Hg)	Temperature (°C)	Wool	Bright Nylon	Dull Nylon	Rilsan	Silk	Dacron
62.5	2.5	7.24	12.43	13.78	9.59		
63.5*	31.0	5.60	10.27	11.61	8.14		
55.3	39.0	4.91	10.75	—	7.54	3.44	
64.4	29.1	5.33	11.60				0.48
55.6	−8.5	7.01	14.06				1.22
After desorption (21 days)							
		1.13	0.71				0.26

* The conditions represent desorption.

Dyed Wool

A sample of wool yarn dyed with Orange II and containing 27% of dye acid based on the dry weight of the original wool was also included in the tests.

Results

The samples were tested under varying conditions of pressure and temperature, but the conditions were not necessarily the same for all samples. Only four samples could be measured at one time in the apparatus and in repeating tests no attempt was made to duplicate exactly the conditions of previous tests, but in the majority of cases a wool sample was included so that this could be used as standard of reference. The results are given in the form of rate of sorption curves in Figures 1–4, while the amount of HCl sorbed at equilibrium is given in Tables I and II.

Figure 1 gives the rate of sorption found for untreated wool and wool treated with alcoholic KOH. There is no significant difference between the two rates of diffusion. The amount of HCl sorbed was also the same within experimental error, namely, 4.31 mM/g for untreated wool and 4.35 mM/g for

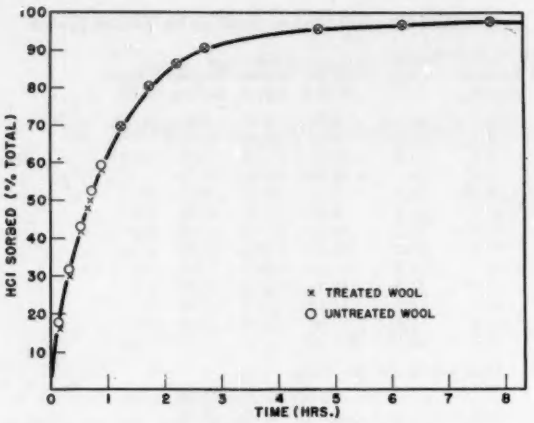

Fig. 1. Rate of sorption of HCl by wool treated with KOH and by untreated wool. Pressure, 51.9 cm Hg; temperature, 41°C.

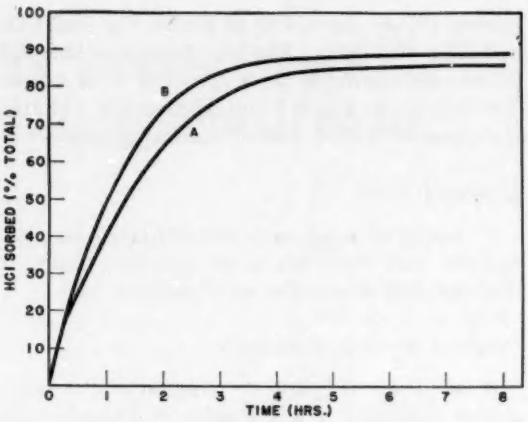

Fig. 2. Rate of sorption of HCl by extracted wool and by untreated wool. Pressure, 46.4 cm Hg; temperature, 30.5°C. *A*, extracted wool; *B*, untreated wool.

treated wool at 41°C and 51 cm pressure of HCl.

In Figure 2 the rate of sorption of untreated wool is compared with that of wool extracted with ether for 2 mo. The results are rather unexpected in that the extracted sample showed a somewhat lower rate of sorption than that of the untreated wool, but the HCl pick-up at equilibrium was practically the same for the two samples, 4.41 mM/g for the untreated wool and 4.45 mM/g for the extracted wool, at 30.5°C and 46.4 cm pressure.

The results obtained with the D.N.B. wool are given in Figure 3. In the low-pressure experiments, 4.6 cm and 5.3 cm pressure, the treated wool sorbed the HCl more rapidly than did the untreated wool. The D.N.B. silk also showed a more rapid rate of sorption than the untreated silk. In the high-pressure experiments, however, i.e., at a pressure of 52 cm, the rates were not appreciably different for the treated and the untreated samples. A sample of wool yarn dyed with Orange II and containing approximately 27% of dye based on the original dry wool weight was also included in the series of tests at 52 cm pressure. Its rate of sorption is not shown in Figure 3, but it was a little below curve *B*, and somewhat lower, therefore, than the corresponding rates for the intact wool and the D.N.B. wool. The HCl sorption at equilibrium for these samples is summarized in Table I.

The results obtained with nylon and other fibers are summarized in Table II, which gives the HCl take-up at equilibrium under a variety of temperature and pressure conditions, while Figure 4 illustrates the rate of sorption of nylon and Rilsan as compared with that of silk and of wool under the same conditions.

Discussion

It has been shown by Lindberg [7] that the rate of diffusion of dyes and of acids from aqueous solutions into wool fibers is increased when wool is treated with an alcoholic KOH solution. This apparently is the result of changes produced in the epicuticle. However, the increase was not so pronounced for HCl as for a number of dyes. The results given in Figure 1 show that no such increase is evident in the case of gaseous HCl. The difference in behavior between HCl in the gaseous form and that in aqueous solution is not altogether surprising, since the rates of diffusion calculated by Lagermalm et al. [5] are very much lower than those calculated in Part I for gaseous HCl and indicate different diffusion mechanisms in the two cases.

Lindberg [7] also found that the rate of diffusion of HCl from aqueous solution increased somewhat when fatty matter was extracted from the fiber. Human and Speakman [4] showed that on prolonged extraction of wool with ether an increasing amount of material was removed with time. The results given in Figure 2 show that, contrary to what might be expected, the rate of diffusion through the extracted wool was slower than that through the untreated wool.

It is difficult to account for this unexpected result unless one assumes that the prolonged extraction closes up the structure of the wool and thus renders the penetration of the HCl more difficult. Such an effect might also account for the higher breaking strength of the extracted wool found by Human and Speakman [4]. If a more open structure facilitates the sorption of the HCl, then the higher diffusion rate shown by the D.N.B. wool at low pressure, Figure 3, could also be explained on this basis since the D.N.B. wool would be expected to have a more open structure than that of untreated wool. It must be noted, however, that in the tests conducted at higher pressures there was no significant difference in rates between the D.N.B. wool and the untreated wool. It would appear from these results that the sorption is a two-stage process and that the first stage, which is prominent at low pressure, is overshadowed by the second stage, which is prominent at high pressure. The D.N.B. silk also sorbed the HCl more rapidly than the untreated silk, although the pressure in this case was comparatively high.

The equilibrium sorption figures given in Table I show that the groups which react with the D.N.F.B. reagent, mostly amino groups, are responsible for only a minor proportion of the HCl sorbed. One is forced to conclude as in Part I that the sorption of HCl is due primarily to the peptide linkage —NHCO—.

It was postulated by Green [3] that the hydroxyl groups in serine and threonine reacted to form the corresponding chlor derivatives, and he used this to explain the difficulty of removing all the sorbed HCl from silk on evacuation. It was pointed out in Part I that on evacuation it was possible to desorb the HCl to a point where the wool contained less HCl than the amount corresponding to the serine and threonine content and that the difficulty lay rather in the very slow diffusion of the HCl under the low-pressure gradient existing under the conditions of desorption. This is borne out by the lower residual contents of the D.N.B. silk and D.N.B. wool. If the rate of diffusion is higher in the treated wool and silk, as indicated by the sorption results, then one would expect that desorption would also be facilitated and that the amount of HCl remaining after desorption would be smaller, as was the case. Further evidence for this is found in the results obtained with the oxidized wool. The peracetic acid used to oxidize the wool presumably affects only the cystine linkage and does not attack the peptide bond [1, 2], which should still be available for HCl sorption. The results given in Table I show that the oxidized wool (α-keratose) has a much higher sorptive capacity than the original wool for HCl, indicating a greater accessibility of reactive sites. This was to be expected in view of the state of fine division of the preparation and the rupture of disulfide bonds holding the chains together. What is of more interest

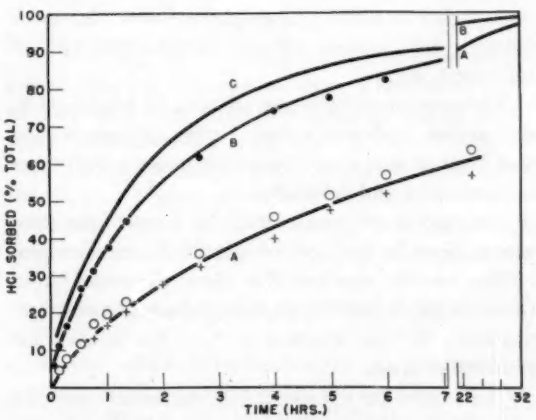

Fig. 3. Rate of sorption of HCl by D.N.B. wool and by untreated wool.

A = untreated wool.
B = D.N.B. wool.
} Pressure = 4.6 cm Hg. Temperature = 41.9°C.

C = untreated wool and D.N.B. wool.
} Pressure = 52 cm Hg. Temperature = 40.8°C.

+ = untreated wool.
○ = D.N.B. blank.
● = D.N.B. wool.
} Pressure = 5.3 cm Hg. Temperature = 42.0°C.

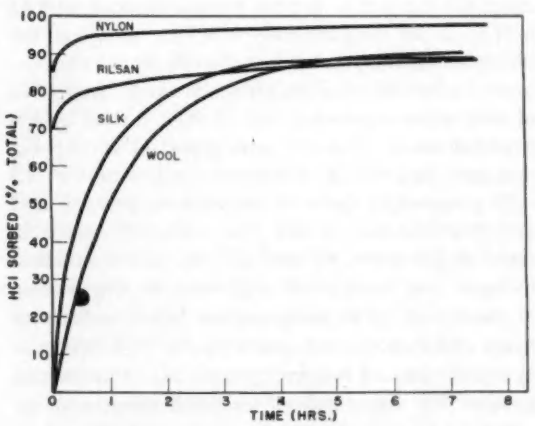

Fig. 4. Rate of sorption of HCl by wool, silk, Rilsan, and nylon. Pressure, 55 cm Hg; temperature, 31°C.

at this point is the negligible amount of residual HCl on desorption, indicating once more that the amount of HCl remaining on the samples on desorption is largely controlled by the slow diffusion.

The sorption of 3.89 mM by the dyed wool (Table I) corresponds to 4.94 mM when calculated on the actual wool content of the sample. This is somewhat larger than the 4.77 mM obtained with the intact wool under the same conditions. It is possible that the dye itself has some affinity for the HCl, e.g., through the diazo group, and is responsible for the difference observed, but the difference may also be due to new peptide groups having been made available to the HCl as the result of the dyeing treatment.

The results in Table II for nylon and other fibers again point to the peptide linkage as being responsible for the HCl sorption. Dacron and Orlon have comparatively small sorptive capacities for HCl, since they contain no peptide grouping. The nitrile group of Orlon might be expected to react with some HCl, but, apparently because of some steric factor, the HCl is not able to reach it.

The high sorption shown by the nylon type of fiber is striking. Under the optimum conditions used in these experiments, 1.5°C and 61.6 cm pressure, Perlon sorbed as much as 61% HCl and nylon 52.3% by weight. Since nylon has ∽ 8.85 mM peptide groups per gram, one must conclude that each peptide link is able to sorb more than one HCl molecule. The attractive forces may be polar but formation of hydrogen bonds is also possible. Further experiments are necessary before one can decide on the most likely mechanism for the sorption process. Since the number of peptide groups in wool, ∽ 8.75 mM/g, is not very different from that of nylon, the difference in the results must be due to a lower degree of accessibility of the groups in wool. Indicative of this is the higher amount of HCl sorbed by the oxidized wool. The 9.1 mM/g sorbed at 11.8 cm pressure and 41.5°C compares well with the 9.3 mM/g sorbed by nylon at the same temperature and under a pressure of 8.7 cm. The difference in pressure between 11.8 and 8.7 cm. is not sufficient to cause any appreciable difference in the take-up of the nylon. The difference in behavior between nylon and Perlon is also probably due to a difference in accessibility of reactive groups. It is interesting to note that the sample of undrawn nylon gave results which differed little from those obtained with the drawn nylon, thus showing that orientation of the polymer chains has little influence on the amount of HCl sorbed. The dull nylon had a somewhat higher sorption than the bright nylon, indicating that the delustering agent increased the accessibility of the active groups.

The number of peptide groups calculated from the Rilsan structure is 5.46 mM/g. This is 0.62 of the number in nylon. On comparing the sorption of Rilsan (dull) with that of dull nylon, we have a ratio of 0.67, which is fair agreement with the ratio of peptide groups considering that the accessibility may be different in the two fibers.

The lowest degree of accessibility seems to be shown by silk. The number of peptide groups in silk (12.8 mM/g) is higher than that of the other fibers examined; yet silk has the lowest sorption.

These experiments are being pursued further and the results of some recent tests to be published later bring added evidence for the role played by the peptide groups in HCl sorption.

Summary

The sorption of hydrogen chloride by wool has been measured and compared with that of wool treated with alcoholic KOH, with wool which had been subjected to prolonged ether extraction, with wool treated with dinitrofluorbenzene, with dyed wool, and with α-keratose obtained by precipitation from a dilute ammoniacal solution of wool oxidized with peracetic acid. A comparison was also made between silk treated with dinitrofluorbenzene and untreated silk.

The sorption of hydrogen chloride by bright nylon, dull nylon, undrawn nylon, Perlon, Rilsan, Orlon, and Dacron was also determined under a variety of temperatures and pressures.

The rate of sorption of HCl by some of the samples is given in the form of sorption vs. time curves.

The results confirm the view expressed in a previous paper that the peptide linkage is mainly responsible for the sorption of HCl by protein and proteinlike fibers.

The results are discussed with particular reference to the accessibility of the reactive groups in the various fibers examined.

Acknowledgment

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of nylon, Dacron, and Orlon, and to the Société Organico, France, for a sample of Rilsan.

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The Breaking of Single Cotton Fibers under Various Conditions

Ray L. Pearson, Albert G. Funk, and Henry Eyring

Abstract

Values for percentage elongation at break and average force at break of single cotton fibers immersed in water at various temperatures and in various concentrations of NaOH have been determined by statistical methods. A maximum value of average force in 1 *M* NaOH is explained by a cooperative effect of the fibrils.

Introduction

In studying the breaking phenomenon of single cotton fibers, it is useful to make a statistical study of the results from many fibers. Each fiber has individual characteristics with no two fibers the same. Soil conditions, temperature, humidity, maturity of the fibers, etc., each affect its structure.

Because of the time involved in breaking enough single fibers to obtain a statistical average, other experimental methods of study are ordinarily used to determine the physical properties of fibers [3, 7, 8, 11, 14].

Studies which have been made on the breaking strength of single cotton fibers include those by Barratt [1], Brown [2], Meredith [9], Grant [4], and Slater [12].

Experimental Method

The apparatus used in this study was a modified version of the Sookne-Rutherford autographic balance [13]. A constant rate of elongation is applied to the fiber. A chainomatic balance, operated electronically, keeps the force balanced at all times. The force is recorded on a rotating drum by a pen attached to the balance chain. A diagram of the type of curve observed is shown in Figure 1. A detailed description of the autographic balance can be found in a technical report No. XXXV on research contract N7-onr-45101 [6].

The strength of cotton fibers is sensitive to relative humidity (R.H.). It has been shown that above 66% R.H., the tensile strength is almost constant [2]. For this reason, the cotton fibers were soaked for 48 hr in distilled water, long enough to be sure that the fiber was saturated. The single fibers were cut from their seed, care being taken to insure the fibers were not stretched or bruised. Each fiber, with lengths ranging from 1 to 3 cm, was attached to a glass hook and a copper wire by means of Acryloid A-10 (Rohm and Haas), a quick-drying acryloid resin, and then placed in the water bath in a position such that there was no strain on the fiber. A chamber filled with a liquid medium in which the fiber strength was being tested rested on the balance

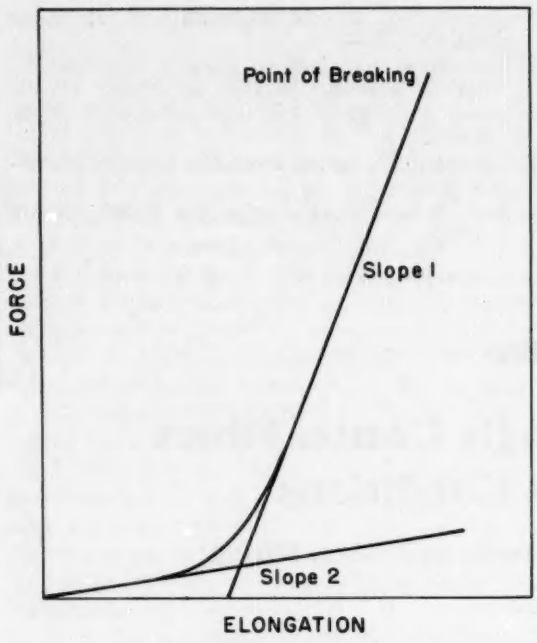

Fig. 1.

pan. The fiber was immersed in this medium, which was thermostated at the desired temperature. The fiber was then elongated at a constant rate until rupture occurred. All the samples were seed cotton from the following stocks: Upland Cotton Strain No. 234 grown at Las Crucas, N. M. (1949); grade: Strict Middling or Good Middling. These samples were supplied through the courtesy of Dr. Carlyle Harmon of the Chicopee Mills, Chicopee Falls, Massachusetts.

Results

The results reported in this article have been obtained by a careful statistical treatment of approximately 100 units broken (N, Table I) in each media. Those interested in the procedure used in the statistical analysis may obtain a report giving the details [10].

In Table I are reported the percentage elongation at break and the average force in grams at break for fibers under various conditions. The large limits of uncertainty which were obtained for percentage elongation at break (close to 10%) indicate that we must use our results in a qualitative rather than a quantitative manner.

Plotting force of breaking against statistical frequency of breaking seems to give no correlation. At the fiber elongations corresponding to slope 1 of Figure 1, all flow within the fiber has ceased and only linear stretching remains, or

$$f = kd$$

In this equation f is the force applied and d is the distance of stretch. The associated force constant is directly proportional to the cross-sectional area. Thus, a thick fiber gives a large force constant; a thin fiber, a small force constant. If fibers had no growth imperfections, f plotted against the slope would equal some constant. Actually, if one plots f vs. slope, a shotgun pattern is obtained. Taking f/slope, normalizing, and plotting the results on top of the theoretical normal distribution indicate there is an average imperfection or nick in the fiber at which the break occurs most often and about which breaking follows a normal distribution.

This viewpoint substantiates the work of Peirce [2] and his coworkers, who found that the average tensile strength of cotton fibers at the third break was double that at the first, while at the sixth break, it was triple. Meredith [9], in comparing the breaking load of cotton and rayon fibers, showed that the coefficient of variation of cotton and rayon was 46 and 20, respectively. This indicated that a manufactured fiber such as rayon when spun by spinnerets produces a fiber with fewer imperfections than a naturally grown fiber such as cotton.

Discussion

According to Table I, the breaking strength of single cotton fibers increases as the fiber is shifted from immersion in pure water media to immersion in 1 *M* NaOH media. However, with still further increase in the alkali concentration, the breaking strength decreases. As the first highly stressed hydrogen bonds are eliminated by alkali, the load is distributed more evenly between all the fibrils, which now align more nearly parallel to one another. A maximum load is carried at a NaOH concentration close to 1 *M*. This increased orientation of the cel-

TABLE I

Medium	Per Cent Elongation at Break ($\bar{X}$)	Limit of Uncertainty (P_s=0.9)	Average Force (g)	N
H_2O—30°C	13.50	13.50 ± 0.54	3.333	93
H_2O—60°C	12.99	12.99 ± 0.59	2.868	92
1 *M* NaOH 30°C	13.68	13.68 ± 0.64	4.243	116
2 *M* NaOH 30°C	13.80	13.80 ± 0.54	3.783	104
4 *M* NaOH 30°C	15.60	15.60 ± 0.62	3.327	94

lulose molecules in NaOH has also been deduced from X-ray investigations [5].

Table I also indicates that with increasing concentration of alkali the percentage elongation at break increases. This increasing elongation arises from the lubrication properties of the alkali due to the hydrogen bond breaking.

Both our experimental data and that of Brown et al. [2] show that with increasing temperatures single cotton fibers saturated in a water media progressively lose their strength. Our data, which extends the temperature range of work begun by Brown, indicates that somewhere between the temperature of 10.3°C and of 60°C there is a maximum in the percentage elongation at break. It appears to be close to 30°C. The water molecules penetrate the fiber to a greater extent as the temperature increases, increasing the lubrication between fibrils. Because higher temperature speeds up breaking of bonds faster than it speeds up the remaking of bonds necessary for elongation, we have a decrease in elongation at breaking at the higher temperatures.

Acknowledgments

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The Oxidation of Wool by Inorganic Peracids

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Introduction

During the past few years considerable interest has been shown in methods for rendering wool keratin soluble. The macromolecular structure of wool is stabilized by the presence of disulfide cross-linkages and becomes soluble in nondestructive solvents, such as weak alkalis or urea solution, only when these linkages have been broken. This may be achieved either by their reduction to sulfydryl groups or by oxidation to sulfonic acid residues. Reduction may be brought about by sodium bisulfite [11] or sodium thioglycollate [12] and may be followed by alkylation [9] to prevent reoxidation of the labile sulfydryl groups.

The most convenient and specific reagent for the oxidative fission of the disulfide bonds in wool is peracetic acid [2, 3], although recent work [6] has shown that the reagent is not as specific as was formerly thought [4].

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After oxidation with peracetic acid, 90% of the wool becomes soluble in dilute ammonia solution. The relationship the residue bears to the histology of the fiber has been the subject of controversy, but the photomicrographs of Manogue and Moss of cross-sections [10] strongly suggest that it consists of a mass of membranes which originally surrounded each cortical cell.

On acidifying the ammonia extract, a cream-colored solid representing approximately 60% by weight of the original wool is precipitated. The soluble and insoluble fractions have been examined by means of their X-ray diffraction and infrared absorption spectra [7, 8, 13], but, whereas it is agreed that the soluble material is in the α-configuration, there is a conflict of evidence as to whether the residue does not, in fact, contain some β-protein.

It has been shown previously that perchromic and pervanadic acids are unreactive toward wool [1], although it is possible that their apparent lack of reactivity is due to their instability. It has now been found that permolybdic and pertungstic acids, which are stable in aqueous phosphoric acid solution, probably with formation of the corresponding heteropolyacid, react with wool in a manner similar to the lower aliphatic peracids and may be used for solubilizing keratin.

Conditions for Oxidizing Wool with Permolybdic and Pertungstic Acids

To oxidize wool with these peracids, the wool (3 g dry weight of scoured and solvent-extracted fibers) was stood for 20 hr in an aqueous solution (60 ml) containing phosphoric acid (30 g H_3PO_4), hydrogen peroxide (1.3 g H_2O_2), and either ammonium molybdate, sodium tungstate (Na_2WO_4), or sodium paratungstate ($Na_{10}W_{12}O_{41}\cdot 28H_2O$, 0.5 g). With permolybdic acid the reaction is preferably performed at 25°C, while with pertungstic acid 18°C may be used. The oxidized wool, after washing, was stirred with 0.20 *N* ammonia solution (300 ml) until it had disintegrated. After filtration from a gelatinous residue, the clear yellow filtrate yielded a curd on acidifying. The residue was oxidized as before and again extracted with ammonia solution. The extract yielded further material on acidification. The total precipitate from the ammonia solutions represented 50–60% by weight of the original wool, while the final residue represented 10–15%.

To confirm that the oxidation was due to the peracid and not hydrogen peroxide, wool was treated exactly as described, but with no molybdate or tungstate in the solution. The wool was apparently unchanged and 98–100% of it was insoluble in 0.20 *N* ammonia solution.

In appearance, the two fractions isolated from wool as described are identical with similar fractions which may be isolated from wool oxidized with peracetic acid. The resemblance between the residues is particularly marked, as in both cases they are very highly swollen, gelatinous longitudinal structures.

In some experiments, after the wool had been oxidized with permolybdic acid the curd precipitated from the ammonia solution was not the usual cream color but was heterogeneously stained blue. This appeared to be due to combination of the molybdenum with the keratin, as X-ray examination showed that the side-chain spacings were affected.

Examination of Fractions by X-Ray Diffraction

The instrument used was a Newton Victor Raymax X-ray apparatus, using high-intensity copper Kα radiation from a rotating copper anode.

Specimens of soluble fractions were prepared by casting films from dilute aqueous ammonia and allowing the solvent to evaporate at room temperature. Fiber residues were prepared by allowing them to dry on a glass plate in a parallel state. No particular difficulty was experienced in preparing samples since they were perfectly satisfactory even when 0.5 mm thick.

The photographs of all the fractions examined showed reflections at 10.0 A, 5.1 A, and 4.2 A. The first two of these, at least, are typical of the α-configuration of proteins of the *k-m-e-f* group and are associated with the side chain and repeat distance along the chain respectively. A fourth reflection, common to the photographs of the insoluble residues, was at 4.4A. This was also present in most of the photographs of the soluble fractions, but in the latter case it was weaker and tended to be obscured by a diffuse band of scatter in this region.

Some specimens of the soluble fractions obtained from wool oxidized with permolybdic acid were stained blue and showed slight modifications from others. Thus they gave a side-chain spacing at 8.9 A with a weaker reflection at 7.4 A, whereas others gave the normal side-chain spacing of 10.0 A.

Neither of the insoluble residues gave any indication of a reflection at 4.65 A associated with a

β-protein, which is normally observed with residues obtained from wool oxidized with peracetic acid.

Examination of Fractions by Infrared Absorption

The specimens, which were examined on a Grubb-Parsons double-beam spectrometer in the range 2–15 μ, were prepared by the same methods as were those used for the X-ray examination, but it was essential that they were much thinner (approximately 10 μ).

All the spectra obtained were similar, having a single peak at 1650 cm^{-1} with some evidence of a double peak at 1545 cm^{-1} and 1525 cm^{-1}. The peak at 1650 cm^{-1} is characteristic of the α-configuration and had any material in the β-configuration been present another peak at 1630 cm^{-1} would have been expected [5]. This latter peak was not found, and it must be concluded that no β-material was present.

The reason for the double peaks at 1545 cm^{-1} and 1525 cm^{-1} is obscure, but they also occur in the ammonia-soluble fractions from peracetic acid oxidized wool, when all the evidence points to this fraction being in the α-configuration. It is very doubtful whether the peak at 1525 cm^{-1} can be assigned to a β-configuration, since orientated films of the soluble fraction from peracetic acid oxidized wool show little dichroism of this peak when examined by polarized infrared radiation, whereas the peak at 1545 cm^{-1} shows marked α-type orientation.

In all the four specimens examined peaks were observed which are believed to be characteristic of sulfonic acid groups and have been observed previously both in wool oxidized with peracetic acid and in cysteic acid itself [14]. This indicates the disulfide bonds of the cystine residues have been oxidized to sulfonic acid groups.

Summary and Conclusions

It has been shown that permolybdic and pertungstic acids in aqueous phosphoric acid react with wool in a manner very similar to peracetic acid. After oxidation, up to 90% of the wool becomes soluble in dilute ammonia solution, leaving a residue of highly swollen gelatinous membranes. From the ammonia solution a protein representing 50–60% by weight of the original wool is precipitated by the addition of acid. The latter is usually cream colored, but when the wool has been oxidized with permolybdic acid it may be blue. This may be analogous to the formation of the wool-chromium complex.

Examination of the fractions by X-ray diffraction and infrared absorption methods has shown that both the soluble protein and the insoluble residue are in the α-configuration. Evidence for the presence of material in the β-configuration in the latter was completely lacking, although a thorough examination of the spectra was made to determine if any were present. These results are in contrast with those given by peracetic acid oxidized wool, because although the soluble fraction is indisputably in the α-configuration [7, 13], there is evidence that material in the β-configuration is present in the insoluble fraction [8].

These reactions provide a link between the organic and the inorganic peracids, in that up to the present they constitute the only methods for rendering wool soluble in dilute solution from which it may be reprecipitated in the α-configuration.

Acknowledgments

Two of us (T. P. M. and G. J. W.) are indebted to the Wool Textile Research Council for fellowships, while one of us (K. S.) wishes to thank the Directors of Messrs. Wolsey, Ltd., Leicester, England, for permission to publish this work.

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Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Behavior of Yarns Subject to Impact Loading

RESEARCH LABORATORIES, ROHM & HAAS CO.
Philadelphia 37, Pa.
July 14, 1955

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Stone, Schiefer, and Fox [6] have recently described some ingenious experiments relating to the behavior of yarns under impact loading. Among other results, they show, as others had shown earlier [5], that when nylon filaments fail under these conditions the new ends have been fused.

They suggest that the cause of fusion may be ". . . the high, localized energy released by bond rupture." We would like to suggest that fusion or pyrolysis is rather a normal concomitant of impact failure and perhaps other types of failure as well.

We have discussed the problem of the energy-absorption capacity of materials in terms of the density of strain energy and the strained volume [3]. If a material "work hardens" in response to strain, when a strain is initiated at a point it will tend to become general so that the strained volume will be large. On the other hand, if "work softening" occurs, the strained volume will remain small and the net energy absorption (the product of the energy density and the volume) will be small. We think that this point of view provides some new insight into the nature of brittleness and toughness as well as providing an explanation of the fusion that is observed in the case at hand.

In the present connection, the impact test is by its nature adiabatic. A work-softening process which must be considered, therefore, is the reduction in modulus that accompanies the work-induced temperature rise. In a qualitative way the importance of this work-softening process is shown by a consideration of the temperature-modulus relationships for various materials given by Schmieder and Wolf [4].

For example, polystyrene, which has a very sharp drop in modulus at the glass temperature, is a brittle material. Nylon, on the other hand, has an attenuated temperature-modulus curve that depends on the existence of crystalline regions which function as crosslinking points in the rubbery material above the glass temperature. Nylon is, of course, an excellent example of a tough substance. Other similar examples can be given, and no exceptions to this general relationship between the temperature-modulus dependence and the toughness of uncrosslinked homopolymers have been found.

The implication of this argument is that failure is a local catastrophe which may involve only a small fraction of the gross sample volume. This concentration of the strain energy at the point of failure can easily lead to fusion or pyrolysis.

For nylon the strained volume is sufficiently large so that the fusion is apparent on inspection. The more brittle materials may fuse over so small a volume element that special methods would have to be devised to detect it, or, indeed, local pyrolysis may be involved.

The development of high local temperatures during the mechanical working of materials has been clearly shown in experiments which involve less violent processes than actual failure. For example, Brauer and Müller [2] have found temperature rises of about 70°C occurring during the drawing of polyvinyl chloride fibers. Bowden and others [1] have observed temperature rises of hundreds of degrees when materials are rubbed together. Fusion was also found in these rubbing experiments.

It should be pointed out that work-softening processes other than those associated with the adiabatic processes can be important. In particular the dependence of modulus on time and on strain should be considered [3].

I. J. GRUNTFEST

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Correlation of the Physical Properties of Jute Yarn with the Chemical Characteristics of the Fiber

TECHNOLOGICAL RESEARCH LABORATORIES
Indian Central Jute Committee
Calcutta 40, India

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In an earlier communication [3] from this laboratory the results of chemical analysis of 28 *capsularis* jute and 22 *olitorius* jute fibers have been published, giving the percentages of nitrogen (N), alcohol-benzene 1:1 extract (F), weight loss on boiling in $N/2$ NaOH (H), "fiber" cellulose after ClO_2 bleaching (C), lignin (L), and ash (A). The corresponding physical properties of yarn, quality ratio (Q), defined as 100 × breaking load (lb) of 10 lb yarn/grist (lb per 14,400 yd), and irregularity (V) measured by the coefficient of variation of the weights of 2-in. pieces were also given. But instead of a complete correlation analysis the authors aimed at the possibility of prediction of Q from chemical characters without reference to the variety of jute, which is often unknown. They obtained regression equations and correlation coefficients from the combined data of both *capsularis* and *olitorius* varieties.

A fuller statistical analysis of the above-mentioned data has now been made in this laboratory.[1] The mean values of Q, V, N, F, and H for *capsularis* having been found to be significantly different from those of *olitorius*; the two varieties have been considered to be two different populations and treated separately.

Of other published results of chemical analysis of different jute-fiber samples, both Norman's [1] and Powrie and Speakman's [2] data suffer from the defects that (*a*) they do not give any quantitative estimate of fiber quality; (*b*) the number of samples analyzed is rather small; and (*c*) figures for nitrogen content, of which the relative variation (*Max-Min*)/*Mean* from sample to sample is more than any other character, and which has been found to be very closely linked up with yarn strength, are not given. These defects make them unsuitable for inclusion in the present analysis.

Some of the results of statistical analysis are given in Table I. The *capsularis* correlations, with the exception of QC, are nearly the same as those ob tained from combined data, while the *olitorius* correlations are different. This confirms the basic difference between the two varieties of jute.

Although N in jute is less than 0.4%, Q bears a significant negative correlation with N. In *capsularis* this correlation coefficient retains its highly significant value even at the fifth-order stage, and in *olitorius* it falls just below the level of significance at that stage; i.e., after the effects of five other constituents are eliminated. This has been explained on the supposition that the contribution of fiber aggre-

TABLE 1. Coefficients of Correlation between Physical Yarn Characteristics and Chemical Characteristics of Jute Fiber

Characteristics Correlated	Simple (Zero Order)			Partial (5th Order)	
	Combined	*Cap.*	*Oli.*	*Cap.*	*Oli.*
QN	−0.88S	−0.89S	−0.59S	−0.81S	−0.37
QF	−0.77S	−0.63S	−0.23	+0.19	+0.02
QH	−0.69S	−0.56S	−0.18	−0.08	+0.07
QC	+0.14	+0.39d	−0.62S	+0.28	+0.45
QL	−0.42S	−0.48S	−0.07	+0.35	−0.01
QA	−0.48S	−0.63S	−0.34	+0.23	+0.04
VN		+0.50S	+0.33	+0.29	+0.30
VF		+0.26	+0.53d	−0.10	+0.00
VH		+0.25	+0.59S	+0.05	+0.50d
VC		−0.02	−0.57S	+0.12	−0.40
VL		+0.26	+0.47d	−0.04	+0.49d
VA		+0.46d	+0.42d	+0.10	−0.45

S = significant at 1% level; d = significant at 5% level.

[1] The complete data is available on request from this laboratory.

gates toward yarn strength is adversely affected, directly or indirectly, by the nitrogen present in jute; a small quantity of N may suffice for the purpose. N in dried jute is possibly in the form of (*a*) dried protoplasm in lumen, (*b*) nonfibrous tissues of barks, and (*c*) inactive bacteria as residue after bacteriological retting. The effects of *a* take place during growth, higher doses of N in manure having been found to reduce the strength of *capsularis* jute; the effects of *b* and *c* are those due to insufficient retting and over-retting respectively, both being known to cause damage to fiber.

The "fiber" cellulose (C), which forms about 85% of the jute fiber, also shows significant positive correlation with Q when *capsularis* and *olitorius* are considered separately. But these correlations lose significance when the effects of other characteristics are eliminated. This is due to the fact that the strength of vegetable fibers depends on the cellulose chain molecules, but it is more on their length than on quantity that the variation of strength depends.

Loss on alkaline boil (H) is partly due to hemicelluloses, which act as incrusting materials between longer chain molecules and increase stiffness and meshiness of fiber, as does lignin (L). This partly explains the significance of positive VH and VL correlations at the fifth-order stage in *olitorius* and negative QH and QL correlations and their loss of significance at the fifth-order stage in *capsularis*.

Multiple correlation analysis shows that the variances of Q explained by the six chemical characters are 81% and 30% and those of V are 10% and 47% in *capsularis* and *olitorius* varieties, respectively. Some regression equations have also been solved. But from the above it is clear that only Q of *capsularis* can be profitably predicted from chemical characteristics.

The chemical characters considered here have been found to be fairly interrelated, some of the simple correlations being as high as 0.75. Only NL, NA, and FH correlations in *capsularis* and the HA correlation in *olitorius* are significant at the fourth-order stage after the elimination of the effects of four other constituents.

Our thanks are due to Dr. P. B. Sarkar, D.Sc., F.N.I., Director, for his keen interest in the work and many helpful suggestions.

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S. B. BANDYOPADHYAY
S. K. MUKHOPADHYAY

Correction

A Study of Blended Woolen Structures, Part I

Myron J. Coplan and William G. Klein

September, 1955 **Volume XXV, No. 9** **Page 743**

Several equations in Part I contain symbols such as $\sigma_T{}^2$ and $S_W{}^2$. The correct interpretation is simply $(\sigma_T)^2$ or $(S_W)^2$, *not* standard deviation of T^2, etc.

In the upper half of Figure 3, the designations 0.02 and 0.06 should read 0.2 and 0.6.

Equation 32 should be $\bar{T}pq/(p^2\sigma_T{}^2 + \bar{T}pq)$.

Page 752, line 3, should be ". . . since perfect correspondence between W_i and pT_i . . ."

M should be n in equation 34, and equation 35 should be

$$1 = \frac{1}{n}\sum \frac{(pT_i - W_i)^2/C^2}{T_i pq/C}$$

On page 753, the definition of q' is $\dfrac{1}{1 + \dfrac{\bar{W}}{\bar{N}}(k/c)}$.

In equations 39 and 40 the terms under the radicals should read $\bar{T}pq/(qc + pk)$.

Equations 41 and 42 contain the symbols σT^2, which should read $(\sigma_T)^2$.

In equations 44 and 45, the closing parenthesis should follow $\sigma_T{}^2$; i.e., $\bar{T}pq$ is a divisor for the entire right-hand side of these equations.

In the Addendum, page 754, last line of the second paragraph, the page reference should read 751.

In equation 11 and in the paragraph following equation 9 T should read $\bar{T}$.

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to
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Requirements for copy conform, in general, with those for other scientific publications. This brief outline is intended to answer some of the questions which are sometimes raised by authors who are unfamiliar with the requirements of this JOURNAL. A more detailed exposition is available and will be sent upon request.

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